

A Study of Structure and Property of Hollow Silver Halide Microcrystal Emulsions

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Abstract

The preparation methods of hollow silver halide microcrystals have been recently reported in the literatures, however the study on their property and application is seldom appeared. In this paper the hollow cubic Ag[Cl,Br,I] and tabular Ag[Br,I] microcrystal emulsions were prepared, and the relation between structure and property of the hollow cubic and tabular AgX microcrystal emulsions compared with the solid cubic and tabular silver halide microcrystal emulsions comprising the same composition of halides was studied by means of SEM, TEM, surface development, chemical and spectral sensitization. The results showed 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 more 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.

Introduction

The silver halide photographic materials have been significantly developed within recent two decades. A series of new kinds of silver halide microcrystals and new organic compounds useful for photography have been provided. The new design and technique of preparing silver halide microcrystals (such as tabular grains, double and multiple structures, epitaxial grains and so on) have played most important role for improving the quality of photographic materials. In the recent years, another novel kind of silver halide called hollow grain has been provided in the publications and patents.

The possibility to design silver halide microcrystals with holes is based on the following contemplation: since the essential reaction processes of silver halide emulsion are almost all occurred on the surfaces of grains, such as chemical sensitization, spectral sensitization, formation of latent image by light exposure, and development of exposed grains. However, the unexposed silver halide inside of grains has been solved by fixing solution to be wasted. The silver halide as hollow grains might prove several advantages, for example: 1) saving the amount of expensive silver (highest can reach 30%); 2) having high ratio of surface area and volume of grain for absorbing more spectral sensitizing dye and more light; 3) having repaid rate of development, because the development can be occurred simultaneously on both the external and internal surfaces. These characteristics will result in increase the sensitivity of hollow silver halide grain emulsion without enhancing the size of grain or with reducing the grain size useful for improving the granularity and resolution.

The methods of preparation of hollow silver halide microcrystals have been reported in the literatures[1-12]. However, the study on their property and application is seldom appeared except in the Iguchi's [2], Urabe's [6] and author's previous papers [8-12]. The purpose of this paper is to study the preparation and property of hollow cubic Ag[Cl,Br,I] and tabular Ag[Br,I] microcrystals emulsions, and the relation between structure and property of the hollow silver halide microcrystal emulsions compared with the solid cubic and tabular microcrystal emulsions comprising the same composition of halides in order to prove the role of hollow structure.

Experimental

Preparation of hollow and solid cubic silver iodochloro-bromide emulsions

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

Preparation of solid and hollow tabular silver iodo-bromide emulsions

At 80°C and pAg = 9.33 the solutions of silver nitrate and potassium bromide were fed in linear increasing rate into the vessel within 10 min to produce tabular AgBr, then the solutions of silver nitrate and potassium bromide with 5mole% iodide were added in linear increasing rate into the vessel to prepare solid tabular Ag[Br,Cl] emulsion.

The portion of obtained tabular grain emulsion was treated by silver halide solvent at 40^0C for several min for creating small holes on the tabular grains.

Surface development

The gelatin removed samples of deliquated hollow and solid unsensitized silver halide emulsions were dropped on the object-plates. After drying the samples were exposed at 220V-60W light source for one sec. The exposed samples were developed with surface developer deliquated by 1:9(developer:water) for 80 sec. The samples of carbon replica were fixed by 50%KSCN solution for 3-5 min to remove the undeveloped Agx, then the samples for microscopy shifted on the copper gauze as support for observing by TEM the location of developed silver fragments on the thin gelatin shells.

Chemical and spectral sensitization

The above prepared hollow and solid cubic, as well as tabular silver halide microcrystal emulsions were digested at 50^oC for chemical sensitization with gold plus sulfur, then added green dye for spectral sensitization.

Results and Discussion

Observation of hollow AgX microcrystals by SEM

The four SEM micrographs of hollow cubic Ag[Cl,Br,I] microcrystals with different iodide contents (0.5, 1.0, 1.5, 2.0 mole%) were shown in the Figure 1. For comparison, the SEM micrograph of solid cubic Ag[Cl,Br,I] microcrystals were shown in the Figure 2.

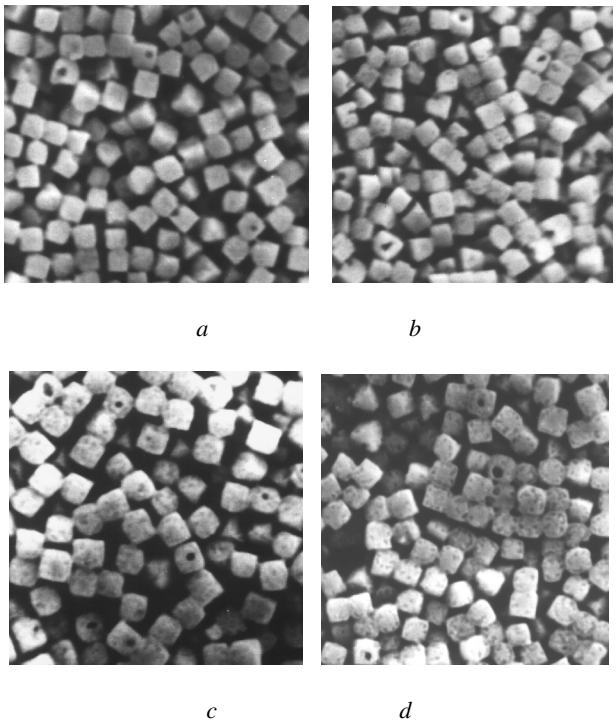


Figure 1. SEM micrographs of hollow cubic Ag[Cl,Br,I] microcrystals with different iodide content (mole%): a.0.5, b.1.0, c.1.5, and d.2.0

From the Fig.1 it can be observed that with the increasing of iodide content added into silver chloride core, the number of microcrystals with hole in center and on the surface is gradually increased. The reason is that bromide and iodide ions are solvent of silver chloride. During the precipitation of silver iodobromide on the surface of silver chloride core, simultaneously the bromide and iodide ions will solve silver chloride to reduce the chloride composition and produce the hole structure.

The compared micrograph of solid cubic Ag[Cl,Br,I] (Fig.2) prepared by conventional method of cubic AgX is exhibited that there is no hole structure existed.

The hole structure of tabular Ag[Br,I] microcrystals treated by solvent is shown in the Fig.3.

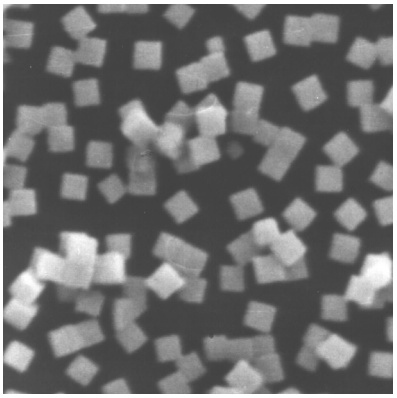


Figure 2 SEM micrograph of solid cubic Ag[Cl,Br,I] microcrystals with 1.5mole I %

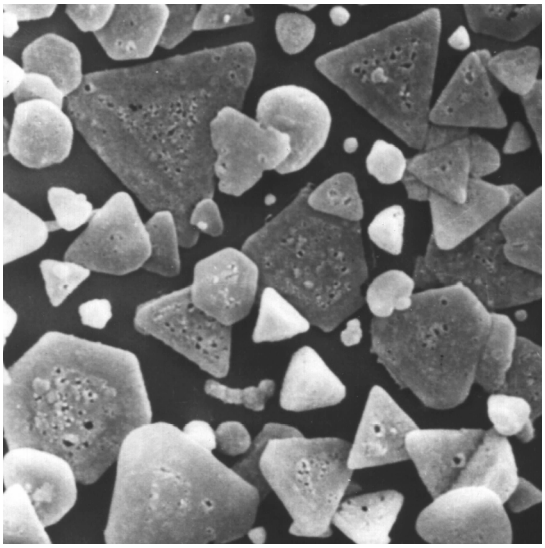
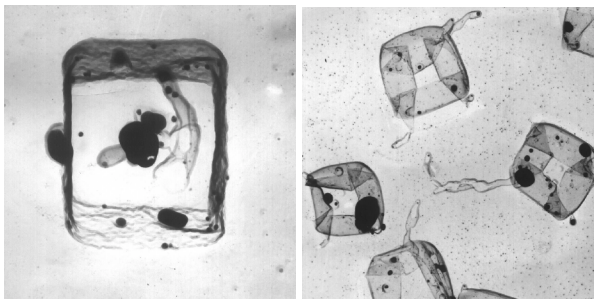


Figure 3. SEM micrograph of hollow tabular Ag[Br,I] microcrystals

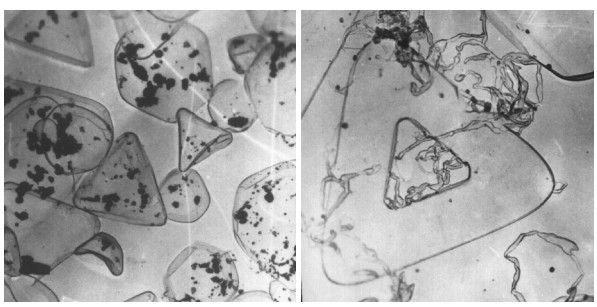
Result of surface development

The experiment of surface development has been carried out to observe the location of initial developed silver filament in order to infer if the latent image center preferentially formed nearby the hole structure of silver halide microcrystal. The TEM micrographs of hollow and solid (for comparison) cubic and tabular AgX after the surface development are shown in Fig.4(a,b) and Fig.5(a,b).



a *b*

Figure 4. The silver fragments micrographs of surface developed hollow cubic AgX(a) and solid cubic AgX(b).



a *b*

Figure 5. the silver fragments micrographs of surface developed hollow tabular AgX(a) and solid tabular AgX(b).

From the Fig.4(a) and Fig.5(a) one can see that the silver filament appeared at the central hole, it means that due to the irregularity of configuration at sites nearby hole of hollow silver halide grains, more electron traps might be provided to form preferentially latent image centers near holes. However, for the solid cubic and tabular AgX microcrystals, the initial silver filaments are always formed at the edge active sites of grains (Fig.4(b) and Fig.5(b)).

Results of sulfur and gold sensitization

The results of surface development proved that the silver filament initially spreaded out from the central hole of hollow grain. It is contemplated that the hole structure of hollow AgX microcrystal may increase the efficiency of latent image formation. In order to evidence the effect of hole structure on the property of emulsion, the sulfur and gold sensitization was carried out for the hollow AgX emulsions. The results were listed in the table 1.

The sensitivities of hollow cubic Ag[Cl,Br,I] emulsions are increased with enhancing of iodide content.

In order to prove the contributions of iodide content and hole structure of hollow silver halide emulsion to the increasing of sensitivity, the chemical sensitization of solid AgX emulsions with the same concentration of iodide was carried out for comparison. From the table 1it showed that the sensitivity of solid cubic emulsion is lower than that of hollow cubic emulsion (c) with the same iodide (1.5mole%). Therefore it illustrated that the hole structure is the mean reason for enhancing sensitivity.

When the reactions of precipitation and replacement are undertook, the chloride ions are replaced by bromide and iodide ions, the hole structures on the grains are gradually appeared. The dislocation and defect near the hole location should be increased; therefore it results in enhancing the efficiency of latent image formation. Moreover, fraction of easy developable silver chloride was remained in the hole site, this is also one of reasons for increasing sensitivity.

The comparison of sensitometric results in table 1 also showed that the sensitivities of hollow tabular Ag[Br,I] emulsions are definitely higher than solid one with the same iodide content.

Table 1. The comparison of photographic properties of hollow and solid emulsions sensitized by S+Au

Emulsions	I mole %	D_o	γ	RS
Hollow cubic Ag[Cl,Br,I](a)	0.5	0.30	2.1	110
Hollow cubic Ag[Cl,Br,I](b)	1.0	0.30	3.6	123
Hollow cubic Ag[Cl,Br,I](c)	1.5	0.30	4.0	188
Hollow cubic Ag[Cl,Br,I(d)	2.0	0.29	2.8	357
Solid cubic Ag[Cl,Br,I	1.5	0.29	2.1	100
Hollow tabular Ag[Br,I]	5.0	0.24	1.5	185
Solid tabular Ag[Br,I]	5.0	0.22	1.2	100

RS: the sensitivity of solid AgX is defined 100

Results of green spectral sensitization

The results of green spectral sensitization of hollow cubic and tabular AgX emulsions compared with that of their solid emulsions are shown in the Table 2.

The results in the Table 2 evidenced again that the hole structure on the hollow cubic Agx microcrystals plays more important role in sensitivity than iodide content. Moreover, the more interesting is shown in the results of tabular AgX emulsions. The purpose of preparing tabular grains is enhancing the surface area for more adsorbing spectral sensitizer to increase sensitivity, however in the present

case, although the surface area of hollow tabular grains due to present holes is decreased, but their sensitivity is still higher than that of solid one with the same content of iodide.

All these facts illustrated that due to the existing of the unique hole structure in silver halide, the photographic property of hollow emulsion is improved.

Table 2. The comparison of spectral sensitivities of hollow and solid emulsions sensitized by green dye

Emulsions	I mole %	Dye Cont .(ml)	D_o	γ	RS
Hollow cubic Ag[Cl,Br,I](a)	0.5	2	0.30	1.9	122
Hollow cubic Ag[Cl,Br,I](b)	1.0	2	0.31	3.1	133
Hollow cubic Ag[Cl,Br,I](c)	1.5	2	0.31	3.9	213
Hollow cubic Ag[Cl,Br,I(d)	2.0	2	0.29	1.7	392
Solid cubic Ag[Cl,Br,I	1.5	2	0.29	1.9	100
Hollow tabular Ag[Br,I]	5.0	6	0.30	2.6	170
Solid tabular Ag[Br,I]	5.0	6	0.25	1.9	100

RS: the sensitivity of solid AgX is defined 100

Acknowledgement

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