Inherently Stable High-Aspect-Ratio Silver Chloride Tabular Emulsions

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A wide variety of silver bromide crystal morphologies can be produced in a straightforward manner by changing the excess bromide level during emulsion precipitation. A number of these conditions produce morphologies bounded by {111} faces, most notably the twinned tabular form. Silver chloride does not inherently lend itself to such a variety in part because the {111} crystal face is not stable without strongly adsorbed growth modifiers. A new type of inherently stable high-aspect-ratio tabular silver chloride has been precipitated by adding small amounts of iodide (less than 0.1 mole% overall) early in the process to induce anisotropic grain growth under low supersaturation conditions. Unlike the traditional twinned tabular morphology, these new crystals possess stable {100} major faces, contain no twin planes, and do not require organic growth modifiers for formation or stability. Photographic performance consistent with the high surface-to-volume ratio, such as high light absorption and covering power, is obtained using conventional methods of spectrochemical sensitization.

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Introduction

Because of their increased surface-to-volume ratio and reduced light scattering, tabular silver halide morphologies show a wide range of photographic advantages such as an improved speed-granularity relationship, increased separation between spectral and native speed, increased developability and covering power, and improved sharpness in the underlying layers of multilayer films.[1] Double parallel twinned silver bromide or iodobromide emulsions are widely used in many commercial film products and are most commonly recognized by the hexagonal to triangular shape of the major face that lies in the {111} crystallographic orientation.

In contrast to silver bromide and iodobromides, silver chloride develops more rapidly and is more easily bleached and fixed, thus providing an overall processing efficiency advantage. Silver chloride emulsions also scatter less light than silver bromide emulsions of comparable size and shape because of the smaller relative refractive index of silver chloride in gelatin.[2]

The precipitation of silver chloride emulsions has historically shown less morphological variety than that of silver bromide. The faces of silver bromide crystals lying in the {100} and {111} orientation are inherently stable; hence, silver bromide forms cubes, octahedra, and a variety of twinned morphologies depending primarily on the excess halide level during precipitation.[3] In contrast, silver chloride precipitations form cubes for much of the range of excess halide conditions owing to the instability of the silver chloride {111} face. Factors such as reduced light absorption and image amplification limit the utility of large grain-size emulsions comprised of low-aspect-ratio morphologies, such as cubes.[4] Other fundamental limitations associated with the latent image-forming steps in larger grain-size emulsions exist in general,[4,5] and in silver chloride cubic emulsions,[6] in particular. As a result, silver chloride has been limited to those applications where high sensitivity and good image structure are not required.

A variety of methods exist for producing silver chloride tabular grain emulsions of the traditional type with parallel twin planes and {111} major faces.[7a–g] These methods employ strongly adsorbed growth modifiers to stabilize the {111} face; such modifiers often restrict the spectral and chemical sensitization process or induce fog. Twinned morphologies with {100} major faces do not have high surface-to-volume ratios and suffer from the deficiencies of low-aspect-ratio emulsions. Inducing anisotropic grain growth without major growth-enhancing defects like twin planes has been difficult. Some low-aspect-ratio silver bromide emulsion grains without twin planes and with {100} oriented major faces have been made using ammonia.[8] High-aspect-ratio silver bromide emulsions of this type have been prepared using an excess bromide-ripening process.[9] Individual grains of low-aspect-ratio tabular silver chloride with {100} major faces have also been observed in various ripening and growth modifier studies.[10a–c]

This paper presents the precipitation, characterization, and photographic response of a new type of inherently stable high-aspect-ratio tabular silver chloride emulsion prepared by using small amounts of iodide early in the precipitation to induce anisotropic grain growth.[11]

Experimental

The typical precipitation process for this new type of high-aspect-ratio silver chloride consists of a double-jet nucleation at 40°C and a pCl of 1.9 to 2.35. For example, a pCl of 2.35 produces an aspect ratio of 14. A low methionine gelatin is used, and iodide ion is present at about 1.5×10^{-4} M to promote anisotropic grain growth. The nucleation is followed by a 10-minute hold to allow ripening, then a double-jet growth with sodium chloride is used to

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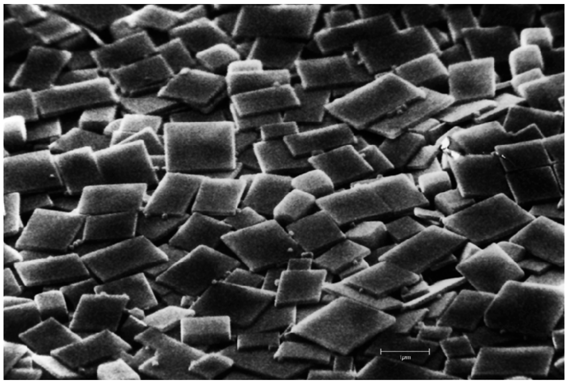

Figure 1. A direct scanning electron micrograph of a high-aspect-ratio silver chloride tabular emulsion where small amounts of iodide were added early in the precipitation to initiate anisotropic grain growth.

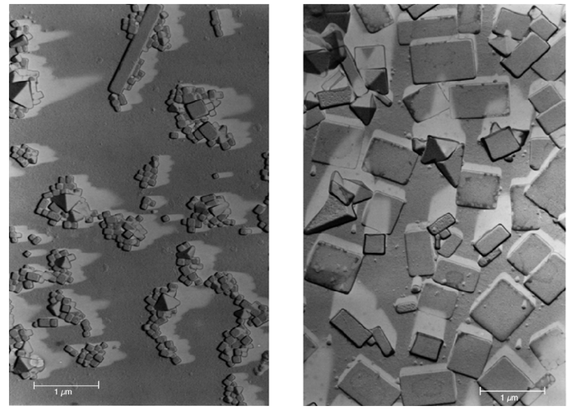

Figure 2. Scanning electron micrographs of the carbon replicas of two silver chloride emulsions identical in all aspects except that iodide was intentionally added at nucleation in the precipitation of the emulsion on the right.

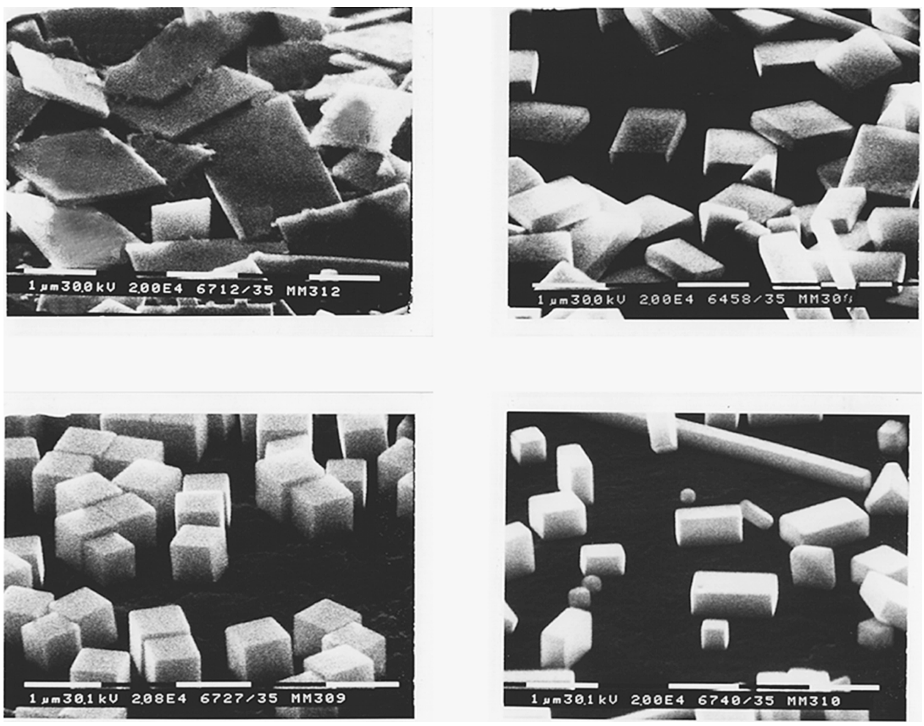

Figure 3. Scanning electron micrographs of a silver chloride cube and three tabular silver chloride emulsions with aspect ratios of 2.5, 4.2, and 14.

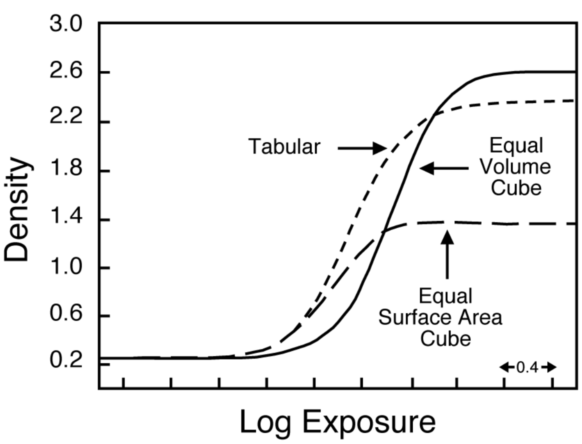

Figure 4. Characteristic curves from a minus blue light exposure and color development of single layer coatings containing a silver chloride tabular emulsion of aspect ratio 13, a silver chloride cube of approximately equal grain volume and one-half the surface area, and a larger silver chloride cube of approximately equal surface area and 4× the tabular grain volume.

maintain a consistent excess halide level. The final iodide content of these emulsions is typically 0.1 mole% or less. The authors have observed that the grain size and percentage of tabular grains are influenced by the nucleation iodide and silver levels, although that is not the focus of this paper.

The aspect ratio can easily be manipulated by varying the excess chloride level during the crystal growth phase of the precipitation. Two emulsions with relatively low aspect ratios of 4.2 and 2.5 were prepared by increasing the excess halide level during growth so that the pCl was 1.6 and 1.2, respectively.

As controls for evaluating the photographic performance of the high-aspect-ratio {100} tabular silver chloride emulsion, two pure silver chloride cubic emulsions were precipitated using conventional double-jet techniques. Of the two pure silver chloride cubic emulsions, one had approximately equal grain volume and half the surface area (0.6-μm edge length) and the other had approximately equal surface area and 4× the grain volume (0.94-μm edge length) of the high-aspect-ratio {100} silver chloride tabular emulsion. The three emulsions were green sensitized using the dye benzothiazolium, 5-chloro-2(2-((5-phenyl-3-(3-sulfobutyl)-2(3H)-benzoxazolylidene)methyl)-1-butenyl)-3(sulfopropyl)-, inner salt, compound with N,N-diethylethaneamine (1:1) and conventional sulfur and gold sources. Optimum sensitizing dye level for the tabular emulsion was 0.7 mmole of dye per mole of silver halide, while the small and large cubes gave maximum speed at 0.2 and 0.15 mmole per mole, respectively.

Characterization

The morphology of this new type of high chloride tabular emulsion can be seen in the scanning electron micrograph shown in Fig. 1. The grains are square to rectangular in shape with aspect ratios to 20 or more. Electron diffraction shows the major faces lie in the {100} crystallographic orientation, and TEM analysis of cryosectioned grains shows no twin plane as would be expected.

The effect of the iodide is illustrated in Fig. 2 showing the electron micrographs of crystals prepared in identical precipitations except for the inclusion of 2 mole% (based on silver added during nucleation) of iodide at nucleation. The final iodide level depends on the extent the nuclei are grown. The emulsion with iodide is comprised predominantly of high-aspect-ratio tabular grains, many with grain thickness below 0.06 μm. A very small number of twinned morphologies with {100} major faces can also be seen. The precipitation without intentionally added iodide is predominantly small cubes.

Figure 3 shows electron micrographs of four emulsions with varying aspect ratios: a cube prepared without iodide at nucleation and at a pCl of 1.6, the two intermediate-aspect-ratio emulsions described above, and an emulsion with an aspect ratio of 14, grown with a pCl of 2.35 similar to that shown in Fig. 1.

Photographic Response

Figure 4 compares the photographic performance of the green-sensitized {100} silver chloride tabular emulsion (aspect ratio 14) to similarly sensitized silver chloride cubes of approximately equal volume or equal surface area. Notice that in reasonable agreement with expectation, an increase in sensitivity by more than a factor of 2 is observed for the larger cube relative to the small cube, with the large cube showing a substantial decrease in gamma and maximum density owing to reduced efficiency of dye formation. The silver chloride tabular emulsion, with twice the surface area of the small cube, also shows about a twofold increase in sensitivity, but the gamma and maximum density are more similar to the small cube as expected from their similar grain volumes.

Summary

A new type of inherently stable, high-aspect-ratio silver chloride tabular emulsion has been precipitated by adding small amounts of iodide early in the process to induce anisotropic grain growth. Unlike the traditional tabular morphology with parallel twin planes, the major faces of these new crystals have a {100} lattice orientation with no twin planes and do not require tightly adsorbed organic growth modifiers or stabilizers. Photographic performance consistent with the high surface-to-volume ratio is obtained using conventional methods of spectrochemical sensitization.

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