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TECHNICAL NOTE

THE PREPARATION AND STRUCTURE OF TABULAR MULTISTRUCTURE SILVER HALIDE MICROCRYSTALS

IN YEONG PARK[1], HONG CHAN AHN[1], MIN YOUNG YOUN[1], YONGEN XU[2] and TAI SUNG KANG[1]*
[1] Industrial Chemicals Division, Korea Research Institute of Chemical Technology
Taejon, 305-606, Korea
[2]Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, China

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Abstract - The tabular multistructure silver iodobromide microcrystal emulsion was prepared by double-jet precipitation under controlled pAg and temperature. The distribution of iodide ions in the microareas of a microcrystal was analyzed by means of Scanning Transimissive Electron Microscope (STEM) and X-ray Energy Dispersive Spectrometer (EDS). The result coincides with anticipated iodide distribution. X-ray line scanned across thinner sample provides a relative accurate technique to determine stratified structure containing different amount of iodide. It will help us improve the preparation of silver iodobromide emulsion.

INTRODUCTION

Silver halide microcrystals are structure sensitive materials. In recent 15 years the interest of study on silver halide emulsion has focused on creating more efficient microcrystal structure to improve the quality of photographic materials.[1-7] Scientists in the field of image science now can design various kinds of microcrystals, for example, core-shell, T-grain, double structure, multistructure, epitaxial and so on.

Multistructure crystals (MSC) have led to color negative films of super-high sensitivity and superb image quality. These films' high latent image formation efficiency results from MSC's charge separation effect and sensitizaton and high adsorption of spectral sensitizing dyes.[4,8,9] Multistructure crystals are multi-layered silver halide crystals whose layers are varied in thickness and AgI concentration to maximize photographic sensitivity[8]. Judging from the scarce literature such systems allow separation of light generated charge carriers;electrons and holes. Iodide ions capture the holes in iodide-enriched areas ; electrons are captured in iodide-depleted areas. This permits the concentration of photoelectrons and subsequently the latent image of the whole bulk or the whole surface on the selective sites. The development starts selectively in the areas with minimum iodide concentration and is inhibited as soon as its front approaches the nearest iodide-enriched areas. Thus the sensitivity depends upon the whole bulk of the crystal, while image granularity and its sharpness(colour and black-white) are affected only by the limited developing areas. Hence, in the systems under consideration it is possible to break the classical balance between granularity and sharpness on one hand and sensitivity on the other.

The purpose of this paper is to prepare tabular multistructure silver iodobromide microcrystal emulsion and to analyze the distribution of iodide ions in the microareas of a microcrystal.

MATERIALS AND METHODS

The silver iodobromide tabular microcrystal emulsions were prepared by double-jet precipitation under controlled pAg and temperature. The grains of emulsion have the multiple structure which consists of pure silver bromide and silver iodobromide, respectively. (Fig. 1)

Preparation of seed crystals. To 0.45 liter of 3.0% deionized bone-gelatin solution containing 0.008*M* potassium iodide and 0.09 *M* ammonium bromide were added with stirring and by double-jet addition a 3.0 *M* NH_4Br solution (at a rate to maintain a constant pAg of 9.6) and a 3.0 *M* $AgNO_3$ solution

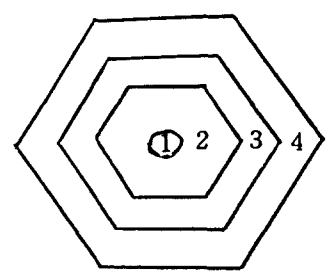

Figure 1. Diagram of tabular multistructure microcrystals. Drawing not scaled for theoretical band width.

* To whom correspondence should be addressed.

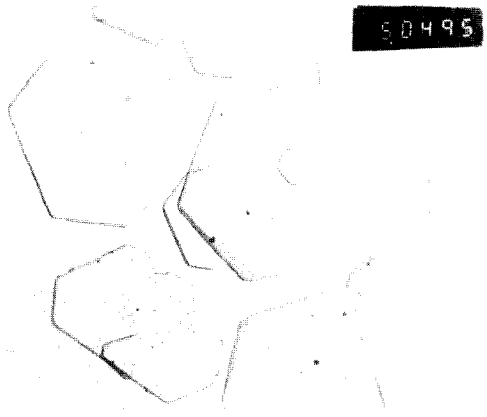

Figure 2. The electron micrograph of AgX microcrystals.

at 3.0 mL/min for 1 min. The rate was then accelerated linerly to 5.0 mL/min. The emulsion was cooled to 40°C. Some kinds of silver halide solvent such as ammonia, were introduced into recrystallization process to avoid renucleation.

Preparation of multistructure tabular silver halide microcrystals. To 500 mL of seed emulsion was added 3.0 *M* $AgNO_3$ solution at 70°C at 4 mL/min for 3 min and were added by double jet addition a 3.0 *M* NH_4Br solution (at a rate to maintain pAg of 9.45) and a 3.0 *M* $AgNO_3$ solution at 2.4 mL/min for 13 min. The rate was then accelerated linearly to 5 mL/min. After 1 min, mixed solution of 2.49 *M* NH_4Br and 0.51 *M* KI and 3.0 *M* $AgNO_3$ solution were added by double jet addition maintaining pAg of 9.45 at 4 mL/min for 8.8 min. The rate was accelerated linerly to 6 mL/min. After 1 min, 3.0 *M* NH_4Br solution and 3.0 *M* $AgNO_3$ solution were added by double jet addition maintaining pAg of 9.45 at 6 mL/min for 15 min. The rate was accelerated linerly to 8 mL /min. The emulsion was cooled to 40°C, washed and stored at pAg of 8.2.

The seed crystals in the beginning of growth step contain 3.4 mol% iodide. Three ring bands of silver halide(silver bromide band, silver iodobromide band and second silver bromide band in turn) were grown outside the seed crystals. The amount ratio of silver in the core to that in three ring bands were 2:24:22:52. The iodide concentration in the silver iodobromide annular ring was 17 mol% approximately. The average diameter of the silver halide microcrystals is 5.0μm.(see Fig. 2)

RESULTS AND DISCUSSION

Iodide content and distribution in silver iodobromide emulsion grains are the important factors in influencing the photographic properties[10]. Analytical Electron Microscopy is a useful technique of determining the microstructure and composition of single microcrystal. In this paper we analyzed iodide distribution in single silver iodobromide microcrystal by X-ray line scan. Analysis of iodide distribution was carried out by using JEOL JEM-200CX Electron Microscope with scanning transmission mode-STEM and EDAX 9100 Energy Dispersive X-ray Spectrometer(EDS) with Edax 9201 Digital Ratemeter

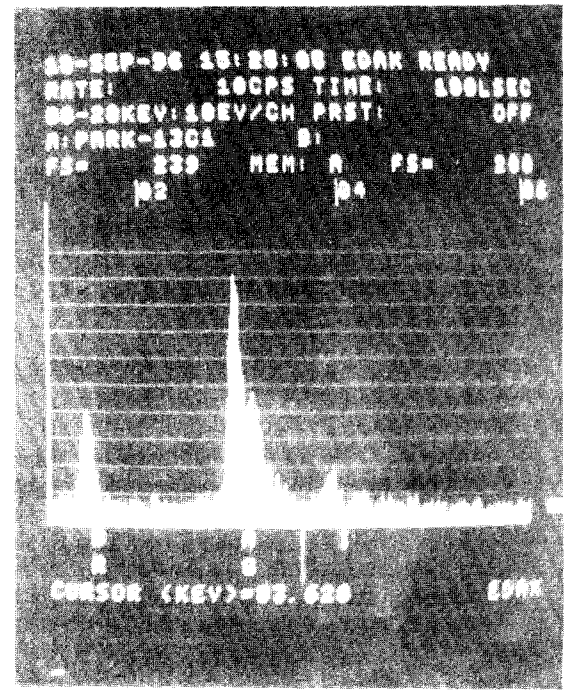

Figure 3. X-ray spectrum of AgBrI microcrystals

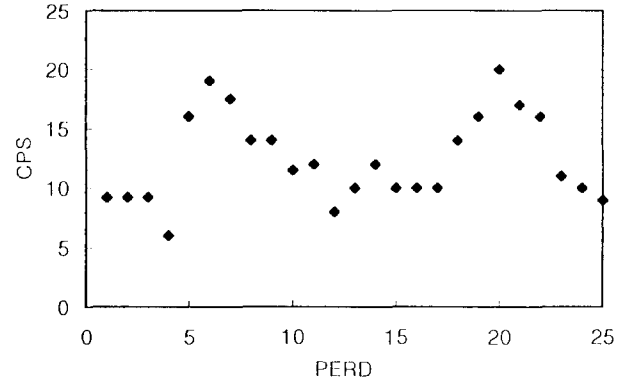

Figure 4. X-ray line scan for Iodine (I La) of AgBrI microcrystal

by the stored line scan mode. While the electron beam is slowly scanned along a line across the specimen, X-ray line scan of interested element can be obtained by STEM-EDS, i.e. the distribution of the element's X-ray intensity (the counters per second, cps) versus the line (expressed in the line scan time or position). The bigger the cps of the element's X-ray, the higher is its concentration. Fig. 3 is a X-ray spectrum of AgBrI microcrystal. We set energy window on iodine peak(I La). X-ray line scan for Iodine was acquired from a single microcrystal when the beam was scanned along the line across the center of the grain from left to right (Fig.4). The grain occupies total integration periods 1-25, and its length is 5.0 μm. This figure illustrates that iodine distribution in the grain has a ring band and there is a

little iodine at the center of the grain. This figure shows that the first and third bands have an iodide content lower than the core and second one. It was found that the iodide ions are distributed in different layers of a tabular microcrystal as designed. The result coincides with iodide distribution of the preparation. X-ray line scan technique can provide a direct and continuous iodide distribution pattern of single silver iodobromide microcrystal. This information will help us study the preparation conditions of silver iodobromide emulsion and the relations between the microstructure and properties of the emulsion microcrystals.

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