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TECHNICAL NOTE

THE STUDY ON THE MICROCRYSTAL GROWTH OF SILVER HALIDE IN PHOTOGRAPHIC EMULSION WITH MODIFIERS

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Abstract—Silver chlorobromoiodide cubic seed emulsion was prepared in the presence of ammonia and phenylcarbamyl gelatin solution. When benzenethiosulfonate sodium salt (BTS) and 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI), as growth modifiers, were added in the seed emulsion, the silver halide microcrystals were obtained in the forms of cubo-octahedrons, octahedrons, rhombic dodecahedron by variation of pAg value through controlled double jet. The crystal habits and shapes were determined by means of X-ray diffraction (D/MAX ⅢB, Rigaku) and electron microscopy (JSM-840, JEOL), respectively.

INTRODUCTION

Various forms of the silver bromide and silver bromoiodide microcrystals have been reported in the presence of organic growth modifiers.[1,2] Typical crystal habit,[6] {111} in octahedral form, {100} in cubic form, {110} in dodecahedral form, were found in silver chloride and silver chlorobromide precipitation by Clase[3] and Mumaw.[4] The organic growth modifiers used are believed to function by particularly strong adsorption to a selective crystallographic plane type, thereby retarding deposition of additional silver halide on it. The slower growth of this plane type relative to that of all the others, would result in a crystal bounded by this type. We observed silver halide microcrystal forms with a silver chlorobromoiodide cubic seed emulsion by variation of pAg value at constant pH in the presence of BTS and TAI which have been used as stabilizer in chemical sensitization[5] as growth modifiers.

MATERIALS AND METHODS

Preparation of $AgBr_{68.5}I_{1.7}Cl_{29.8}$ cubic seed emulsion. To a stirred 1 L of 3% phenylcarbamyl gelatin soltion containing 0.37 mol of $AgNO_3$ and 60 mL of 30% NH_4OH at 45°C was added 210 mL of a mixed solution containing 0.34 mol KBr, 0.15 mol NaCl and 0.008 mol KI.

Preparation of test emulsions. To a stirred solution of AgBrICl cubic seed emulsion at pH 10.4 and at 45°C were added 2.1 *M* $AgNO_3$ and 2.1 *M* KBr solution through a controlled double jet injector at several different pAg with growth modifier. Thus, the solution of 2.1 *M* $AgNO_3$ and 2.1 *M* KBr added to the seed emulsion in the absence of the growth modifier at pAg 7.8 and at 45°C over 80 min, simultaneously. Under the same conditions without growth modifier, the solution of $AgNO_3$ and KBr added to a stirred solution of AgBrICl cubic seed emulsion at pAg 9.0 and 9.6, respectively. On the other hand, 1.6 mmol of the growth modifier TAI added to the seed emulsion (corresponding to $AgNO_3$ 0.29 mol) under the above mentioned conditions, at pAg 7.8, 9.0 and 9.6, respectively.

And 1.0 mmol of the growth modifier BTS added to the seed emulsion (corresponding to $AgNO_3$ 0.29 mol) at pAg 7.8, 9.0 and 9.6, respectively.

RESULTS & DISCUSSION

The average grain size of the $AgBr_{68.5}I_{1.7}Cl_{29.8}$ cubic seed was about 0.6 μm and the crystal habit obtained from XRD was {200}, {400} as shown in Fig. 1. In the seed emulsion without the growth modifier, cubic grains with a crystal habit of {200} as shown in Fig. 2 was abtained at pAg 7.8

But at pAg 9.0 and 9.6, cubo-octahedral with {111}, {200}, {222} and octahedral with {111}, {222} were abtained, respectively (Fig. 3 and Fig. 4).

When the growth modifier TAI was added in the seed emulsion, at pAg 7.8 and 9.0, rhomic dodecahedral grains with {200} were abtained. While octahedral grains with {111}, {222} were obtained at pAg 9.6 (Fig. 5 – Fig. 7).

In the presence of BTS, cubic grains were obtained at pAg 7.8 as shown in Fig. 8, but at pAg 9.0 and 9.6, octahedral grains were obtained (Fig. 9 and Fig. 10).

The results which are obtained from X-ray diffraction profiles and electron microscopy are summarized as Table 1.

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Table 1. Silver halide microcrystal forms and Miller indices obtained from silver chlorobromoiodide cubic seed emulsion in the presence of growth modifiers by variation of pAg

pAg / Modifiers	7.8	9.0	9.6	amount of modifier	
–	Cubes {200}	Cubo-octahedron {111} {200} {222}	Octahedrons {111} {222}	–	
TAI	Rhombic dodecahedrons {220}	Rhombic dodecahedrons {220}	Octahedrons {111} {222}	1.6 mmol	$AgNO_3$ 0.29 mmol
BTS	Cubes {220}	Octahedrons {111} {222}	Octahedrons {111} {222}	1.6 mmol	$AgNO_3$ 0.29 mmol

In the presence of gelatin, ammonia and TAI, BTS as growth modifiers, silver halide microcrystals with new surfaces were obtained in controlled doubel-jet system. The selectivity of organic growth modifiers to inhibit the growth of a specific crystal face type suggests that there is a uniquely strong adsorption between the modifier and crystal face type.

Understanding what makes this interaction unique should enable a better overall understanding of surface adsorption of organics to silver halides.

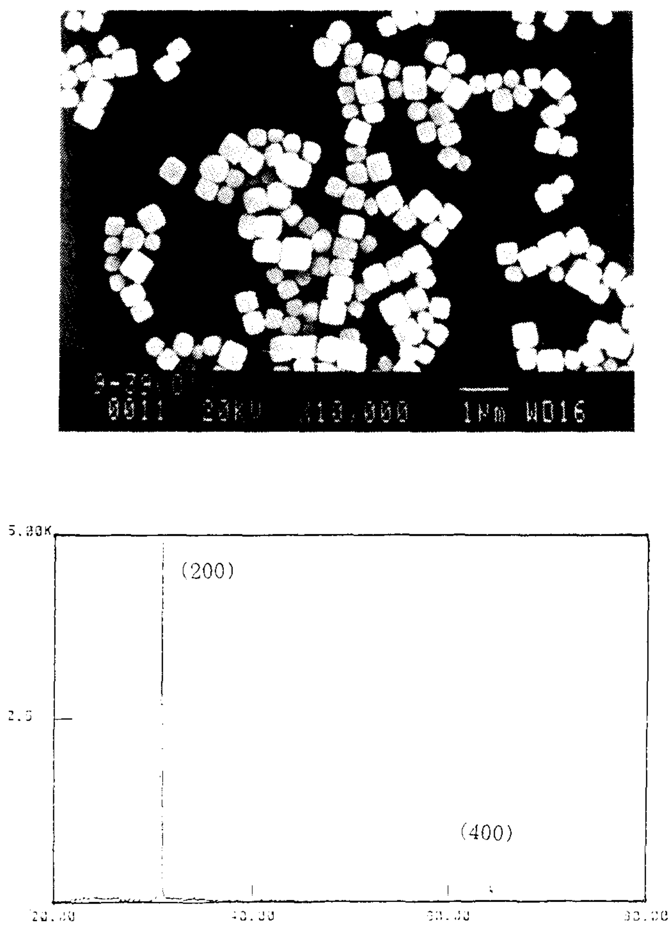

Figure 1. $AgBr_{68.5}Cl_{29.8}I_{1.7}$ cubic seed microcrystals.

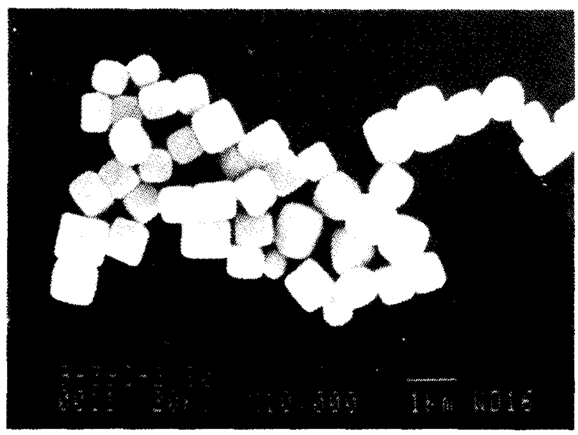

Figure 2. Cubic grains obtained in the absence of the growth modifier at pAg 7.8.

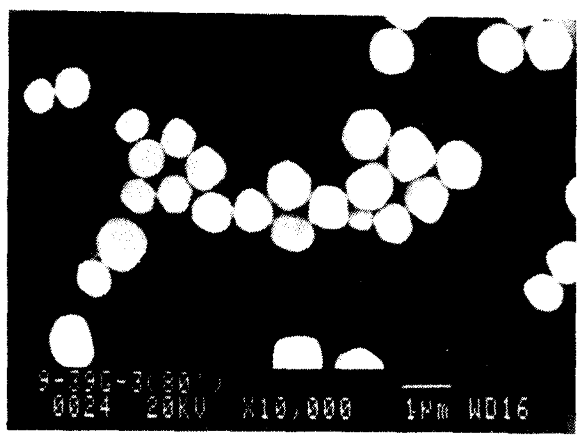

Figure 3. Cubo-octahedral grains obtained in the absence of the growth modifier at pAg 9.0.

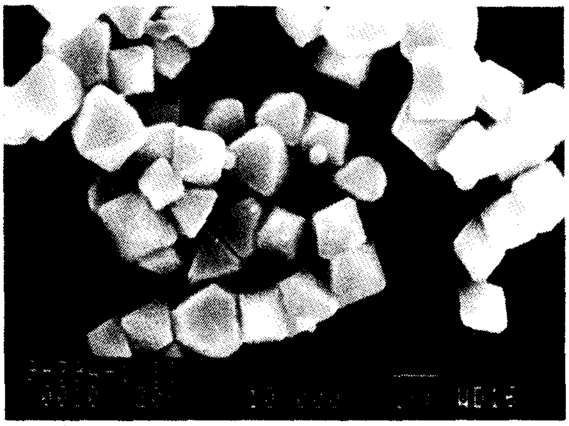

Figure 4. Octahedral grains obtained in the absence of the growth modifier at pAg 9.6.

Figure 5. Rhombic dodecahedral grains obtained in the presence of TAI at pAg 7.8.

Figure 6. Rhombic dodecahedral grains obtained in the presence of TAI at pAg 9.0.

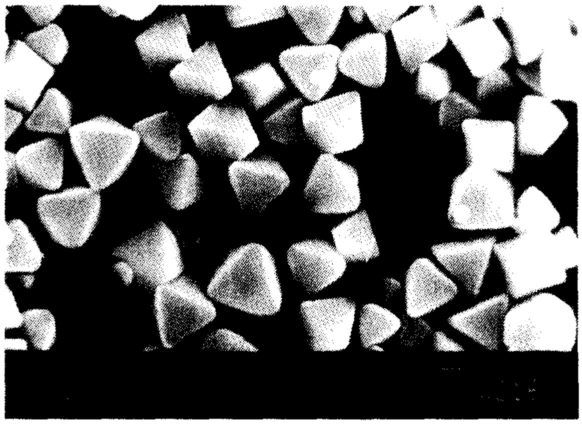

Figure 7. Rhombic dodecahedral grains obtained in the presence of TAI at pAg 9.6.

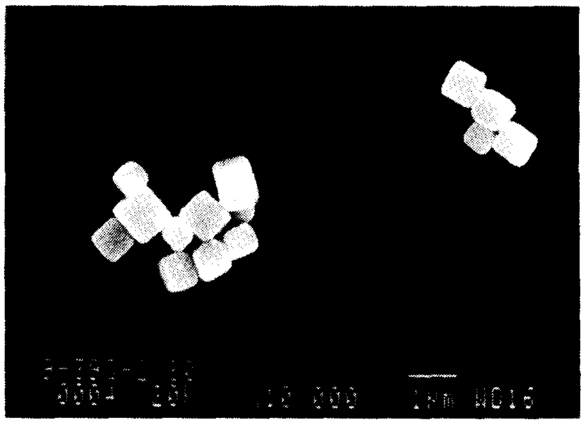

Figure 8. Cubic grains obtained in the presence of BTS at pAg 7.8.

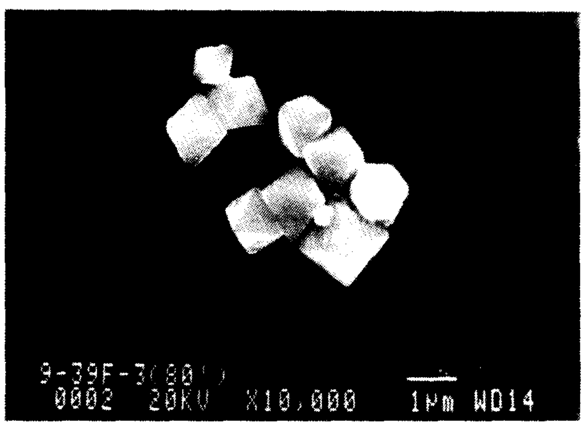

Figure 9. Octahedral grains obtained in the presence of BTS at pAg 9.0.

Figure 10. Octahedral grains obtained in the presence of BTS at pAg 9.8.

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