Study on Preparation and Morphology of Silver Chlorobromide Microcrystals in Photographic Emulsion

Hyun Song, Hyeon Sup Lee, Dong Joo Kwon, Kil Yong Jung, Jong Choo Lim, Euy Soo Lee, Myung Cheon Lee,† and Hyun So Shin

Department of Chemical Engineering, Dongguk University, Seoul 100-715, Korea

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Abstract: The preparation and morphology of silver chlorobromide crystals were studied by double-jetting the reactants into aqueous gelatin solutions. The preparation of cubic crystals of silver chlorobromide was examined by controlling the molar ratio of chloride and bromide ions. When the molar ratio of the two halide ions was 1.0 : 1.75(Cl−:Br−), only cubic chlorobromide crystals were obtained. The presence of a hydrophilic solvent in the aqueous complex solution inhibited the growth of cubic crystals, and converted the cubic crystals to a cubo-octahedron shape with 30 wt% of methanol and ethanol. To study the growth habits of silver chlorobromide crystals, 2-, 3-, and 4-aminophenol silver chlorobromide complexes as a single source precursor for the nucleation of silver chlorobromide crystals were used. The generated silver chlorobromide crystals were cubic, cubo-octahedron, octahedron and tabular in shape. In particular, tabular crystals were only found with the 3-aminophenol reagent, where the crystal size was about 800 nm.

Keywords: silver chlorobromide crystal, morphology, aminophenol, double-jet, tabular crystal

Introduction

Silver halide crystals has been used in photographic emulsions for a long time. Pure and mixed AgCl crystals are normally used for printing materials, such as color papers, black and white papers, lithographs etc., while pure AgBr and mixed crystals are widely used for relatively high-speed photographic materials, such as color negatives, black and white negatives, X-ray films, and instant photography.

In the early 1960s, Ottewill and Woodbridge precipitated monodisperse cubic and octahedral AgBr particles through the decomposition of concentrated AgBr complexes by dilution with water [1]. In contrast, Berry and Skillman developed a new method for the preparation of monodispersed silver halide particles in a much more condensed system, called the "controlled double-jet method" [2,3]. In this system two reactant solutions of silver nitrate and halide ions are continuously introduced with a constant flow rate for the solution of silver ions and variable flow rate for the halide solutions, precisely controlled by a feed-back system including a silver electrode to keep the excess concentration of halide ions at a certain level in the reaction vessel containing gelatin as an anticoagulant [4]. Significant research efforts have been focused on developing new silver halide microcrystal morphologies [5-7]. Theories and methods for controlling the size and shape of silver halide crystals produced during emulsion formation also include discussion of recrystallization phenomena, such as Ostwald ripening [8,9]. The silver halides AgBr and AgCl are well known to have a rocksalt crystal structure with (100) planes under normal conditions. However, if AgBr crystals are grown in excess of bromide ions relative to the concentration of silver ion, these crystals generally have cubo-octahedral and octahedral shapes [10-12].

In particular, if the concentration of bromide ion is further increased, tabular crystals are obtained. The tabular crystal shape is especially interesting for the photographic industry as twinned microcrystals are sometimes claimed to enhance the efficiency of latent image formation [13].

Silver bromide crystals bounded by (100) planes have been grown in the presence of organic additives [14,15]. The use of specific additives can also induce the
apparition of tris-octahedral, tetra-hexahedral, and hexa-octahedral forms [16].

Recently, a side-face structure of tabular silver bromide crystals grown from DMSO [17] and tabular silver bromide, plus silver chloride crystals grown from the vapor phase [18] were observed and explained. A new method for the production of silver bromide crystals from silver halide complex solutions in polar aprotic solvents was also proposed [19-22]. Silver halide emulsions are generally prepared using a reactive precipitation process where aqueous solutions of silver nitrate and alkali halides are reacted in the presence of gelatin. The composition of the resulting product (silver halide emulsion) is controlled by varying the constituents of the alkali halide solution.

In addition, appropriate addenda/dopants are generally introduced into the aqueous solution during the precipitation process, to generate the desired silver halide emulsion compositions [20]. The important feature of all these processes is the bimolecular chemical reaction between the silver cation and the appropriate halide anions to generate the precipitating species. Therefore, it is possible to vary the chemical composition and structure of the product emulsions by varying the constituents of the reagent solution.

The formation of seed crystals was examined with the addition of aminophenol derivatives as crystal growth modifiers. The growth habit and morphology of the resulting crystals were investigated using SEM.

In the current study, silver chlorobromide crystals were prepared in aqueous solutions using a double-jet method in order to investigate the morphology of the crystals. Of particular interest was the effect of the molar ratio of Cl\(^-\) to Br\(^-\) ions, the addition of hydrophilic solvents, such as methanol, ethanol, and acetone, and the morphology changes of the silver halide crystals.

**Experimental Section**

**Materials**

The reagents used for the preparation of the photographic silver chlorobromide emulsion were silver nitrate (99%, Junsei) and gelatin (99%, Merck). The hydrophilic solvents, such as ethanol (99.9%), methanol (99.9%), and acetone (99.5%) were purchased from Aldrich. The organic growth modifiers (2, 3- and 4-aminophenol (99%)) used for the preparation of the silver chlorobromide crystals were supplied from Fluka. The other reagents were all first grade and used without further purification.

**Preparation of Standard Silver Chlorobromide Emulsions**

The silver chlorobromide emulsion was prepared using the simultaneous double-jet method with an equal molar ratio of chloride and bromide ions. To a stirred solution A containing 97 mL of pure water and 5 wt% of gelatin, the solution B and solution C were added at 45 °C.

Solution B contained 50 mL of pure water and 0.6 mol/L of silver nitrate, while solution C contained 50 mL of pure water, 0.3 mol/L of sodium chloride, and 0.3 mol/L of potassium bromide. The physical ripening was continued for 60 min. About 5 min after the completion of the physical ripening the silver chlorobromide emulsions obtained were washed with water for desalting.

**Preparation of Silver Chlorobromide Crystals with Different Ratios of Chloride/Bromide**

Silver chlorobromide emulsions containing different molar ratios of chloride to bromide ions, such as 1.0:0.9, 1.0:0.7, 1.0:0.5, and 1.0:1.3, were prepared by the simultaneous double-jet method. To a stirred solution A containing 97 mL of pure water and 5 wt% of gelatin, the solution B and solution C were added at 40 °C. Solution B contained 50 mL of pure water and 0.6 mol/L of silver nitrate, while solution C contained 50 mL of pure water and different molar ratios of chloride to bromide ions. The injection rate of both the silver nitrate solution B and halide solution C was 1.25 mL/min. The physical ripening was continued for 60 min.

About 5 min. after the completion of the physical ripening the silver chlorobromide emulsions obtained were treated by an enzyme and washed with water. This procedure was repeated three times.

**Preparation of Silver Chlorobromide Crystals in Hydrophilic Aqueous Solution**

Recently, a new method for the production of silver bromide crystals from silver halide complex solutions in polar aprotic solvents was proposed [21,22]. The crystals grown by this method can reach the appropriate size in a short time and can adopt a variety of shapes.

Therefore, to establish the effect of a polar hydrophilic solvent on the growth of silver halide crystals, silver halide crystals were prepared from a complex solution containing a polar hydrophilic solvent, such as methanol, ethanol, and acetone, in the presence of pre-treated gelatin.

The major purpose of this experiment was to investigate the effect of a hydrophilic solvent on the growth of silver chlorobromide crystals. In the experiment, the molar ratio of chloride and bromide ions was fixed at 1.0:0.75.

To a stirred solution A containing 233 mL of pure water and 5 wt% of gelatin at 40 °C, solution B and solution C were added through a controlled double-jet injector. Solution B contained 93 mL of pure water and 0.6 mol/L of silver nitrate, while solution C contained 93 mL of
pure water, 0.33 mol/L of sodium chloride, and 0.21 mol/L of potassium bromide. The physical ripening was continued for 60 min. About 5 min. after the completion of the physical ripening the silver chlorobromide emulsions obtained were used for a SEM photograph.

Solutions A, B, and C were prepared such that each solution contained 5 wt%, 10 wt%, 20 wt% and 30 wt% of hydrophilic solvents, such as methanol, ethanol, and acetone, respectively.

**Preparation of Silver Chlorobromide Crystals Aminophenol Derivative Modifiers**

For the preparation of seed crystals, to a stirred solution A containing 233 mL of 5 wt% gelatin, 0.02 mol/L of silver nitrate and 0.02 mol/L of a growth modifier, such as 2-, 3- and 4-aminophenol compounds, were added, respectively. After 20 min of formation of seed crystals, 93 mL of silver nitrate aqueous solution and 95 mL of a mixed halide solution (95 mL) containing 0.33 mole of sodium chloride and 0.21 mole of potassium bromide were added to solution A.

The physical ripening was continued for 60 min. About 5 min after the completion of the physical ripening, the silver chlorobromide emulsions obtained were treated by pepsin and washed with water for desalting.

**Results and Discussion**

Silver chlorobromide microcrystals were prepared using the double-jet method in an aqueous gelatin solution. The morphology of the crystals obtained was studied by scanning electronic microscopy (SEM). The shape of the crystals varied with the molar ratio of the two halide ions (Cl\(^-\) and Br\(^-\)), the concentration of the hydrophilic solvents, and the presence of aminophenol derivatives as a crystal growth modifier in the solution.

**Morphology of Standard Silver Chlorobromide Crystals**

Standard silver chlorobromide crystals prepared in an equal molar ratio of chloride and bromide ions, silver chloride, and silver bromide were created using the simultaneous double-jet method. As shown in Figure 1, the shapes of the standard silver chlorobromide crystals were cubic(a), cube-octahedron(b), tetrahexahedron(c), and others. The size of the silver chlorobromide crystals prepared by the double-jet method varied from about 0.5 to 0.75 μm.

**Morphology of Silver Chlorobromide Crystals with Different Molan Ratios of Chloride/Bromide**

The effect of the molar ratio of chloride and bromide ions on the crystal size and morphology of silver chlorobromide crystals was investigated. As shown in Figure 2, a significant morphology change in the silver chlorobromide crystals was exhibited depending on the molar ratio of chloride and bromide ions. Cubic, triangular, and trapezoid microcrystals (Figure 2-1) were obtained with a the molar ratio of 1.0:0.3 (Cl\(^-\):Br\(^-\)) and the crystal size varied from 250 to 400 nm. As shown in Figure 2-2, octahedron crystals were found at a molar ratio of 1.0:0.5 and the crystal size ranged from 200 to 400 nm.

As shown in Figure 2-3, more than 90% of the total grain projected area was provided by cubic grains with a (100) plane. Also significant changes in the crystal size were found. When the crystal size varied from 160 to 200 nm, the size of the cubic crystals was inversely proportional to the bromide ion concentration. However, at a molar ratio of 1.0:0.9, the average crystal size was about 500 nm (see Figure 2-4). This increase in the crystal size was due to a change in the crystal shape as most cubic crystals were gradually converted to a cube-octahedral shape at a molar ratio of 1.0:0.9. This behavior was primarily attributed to the growth modifying properties of the multiple halide silver complexes that increased in concentration with an increase excess bromide. Under normal conditions, silver halide crystals (AgCl or AgBr) generally exhibit a cubic structure with a (100) plane. When the crystallization of the silver halide grains took place in an excess of bromide ion, the (111) form was the most stable and the crystals exhibited a cubic-octahedral or octahedral shape [23-25].

**Morphology of Silver Chlorobromide Crystals with Hydrophilic Additives**

**Methanol solution**

As shown in Figure 3-1, most crystals prepared from an aqueous complex solution containing 5 wt% methanol
exhibited a cubic shape with an average size of 250 nm. In the case of 10 wt% methanol, the effect of the solvent was insignificant. However, with 20 wt% methanol, the crystal shape gradually converted from cubic to octahedron (see Figure 3-3). Finally, more than 90% of the total crystal projected area exhibited octahedron crystals with an average size of 200 nm. It would appear that the addition of methanol induced the change in morphology and size of the silver chlorobromide crystals, where the crystal size decreased from 250 to 200 nm.

**Ethanol solution**

As shown in Figure 4-1, most crystals prepared from an aqueous complex solution containing 5 wt% ethanol exhibited a cubic shape with an average size of 250 nm. In the case of 10 wt% ethanol, the effect of the solvent was also insignificant. Even with 20 wt% ethanol, no change in the crystal shape was observed. However, as shown in Figure 4-4, the crystals obtained from a complex solution containing 30 wt% ethanol exhibited an octahedron shape and the size also varied from 250 to 500 nm.

**Acetone solution**

As shown in Figure 5-1, most crystals prepared from an aqueous complex solution containing 5% exhibited a cubic shape with an average size of 250 nm. No significant change in the crystal shape and size was induced by an increase in the concentration of acetone in the aqueous complex solution. This difference in the growth habit of silver chlorobromide crystals in an aqueous complex solution containing acetone was presumably induced by the higher volatility of acetone compared to alcohols.

The morphology of the crystals precipitated from a silver chlorobromide complex solution in organic solvents was studied using SEM. Cubic and octahedron crystals were obtained in this system by solely changing the concentration of the hydrophilic solvent without using any additive. At a lower 30 wt% concentration of hydrophilic solvents the changes in the crystal shape were not significant. However, the average size of the crystals formed in the presence of the hydrophilic solvent was much smaller than in the absence of the solvent. The addition of organic solvents to the aqueous gelatin solution affected the solubility of the silver chlorobromide crystals. As such the rate of nucleation of the silver chlorobromide crystals in the complex emulsion increased, thereby decreasing the crystal size formed.

**Morphologies of Silver Chlorobromide Crystals with Aminophenol Derivative Modifiers**

As shown in Figure 6-1, the use of a 2-aminophenol silver chlorobromide complex as a single source precurisor
for the nucleation of silver chlorobromide crystals did not produce any significant change in the crystal morphology, as the resulting silver chloro-bromide crystals exhibited a cubic structure. However, the crystal size of the silver silver chlorobromide obtained was about 500 nm, which was twice as large as that in the absence of 2-aminophenol. In the case of a 3-aminophenol reagent as the organic growth modifier, a significant change in the crystal morphology was observed. As shown in Figure 6-2, a new tabular crystal shape (see arrow) was produced with the addition of 3-aminophenol into the aqueous solution. Cubic, octahedron, tabular and other silver chlorobromide crystal shapes were also found. The crystal size of a tabular form was about 800 nm. The average size of both the cubic and the octahedron crystals was about 200 nm.

As shown in Figure 6-3, the addition of 4-aminophenol during the formation process of the seed crystals produced octahedron shaped crystals. The average size of these crystals was about 150 nm. The tabular crystal shape is particularly interesting for photographic applications as these crystals are known to have several twin planes parallel to tabular faces [26]. However, the dispositions of their side faces are unclear and the mechanism proposed to explain their formation is still speculative.
Until now, the adsorption mechanism and interaction between the crystal face of silver chlorobromide and an added organic growth modifier have also not been determined. Although the use of a 3-aminophenol silver halide complex as a single precursor for the nucleation of silver chlorobromide produced tabular crystals, the mechanism of crystal growth was not clear. The morphology change in the silver chlorobromide crystals with the addition of a 3-aminophenol reagent suggests a unique adsorption of the modifier onto the crystal face.

Conclusions

The morphology of silver chlorobromide crystals precipitated from aqueous gelatin solutions by the double-jet method was studied using SEM. Both the shape and the size of the crystals varied with the molar ratio of chloride to bromide ions. When the molar ratio of chloride and bromide ions was 1.0:1.75, only cubic crystals were obtained and the average crystal size was 250 nm. When silver chlorobromide crystals were prepared with a polar hydrophilic solvent, the crystal shape varied from cubic to octahedron at solvent concentrations above 30 wt%.

When aminophenol derivatives were added as crystal growth modifiers to aqueous seed emulsions, the resulting silver chlorobromide microcrystals were cubic, cubo-octahedron, octahedron and tabular in shape.

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References