Journal of Photoscience, Vol. 3, No. 3, pp. 159-161

TECHNICAL NOTE

PHOTOSENSITIVITY OF HETEROJUNCTION TYPE GRAINS IN CUBIC SILVER HALIDE MICROCRYSTALS

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(*Received* 28 *October* 1996; *accepted* 13 *December* 1996)

Abstract - Photosensitivity of silver halide emulsion depends on the properties of the microcrystals. Size, shape, grain distribution and chemical composition as well as the inner structure or the topography of the latent image specks affect on the optical properties and play an important role in the photographic process. In the present paper, a study on the sensitization of emulsion containing AgBrClI core/shell grains showed that for the given size, shape, halide content and crystal habit, under the optimal conditions the photosensitivity of the heterojunction type grains are different from that of the common regular grains. The optimal photosensitivity was obtained at the iodide content of 2.0mol%.

INTRODUCTION

It is well known that the size and shape of silver halide microcrystals used in the photographic emulsions concern the dependence of the physicochemical factors such as temperature, ripening time, halide content, pH & pAg. Of these factors, it is certain that pH & pAg values play a very important role in determining the grain shape. Moisar and Klein, using the double jet method[1,2], obtained cubic silver bromide microcrystals at pAg values greater than 7.5 and octahedral microcrystals at pAg values smaller than 8.5. In the range of pAg values between 7.5 and 8.5 face types are stable, and tetradecahedral microcrystals were obtained[1,2]. Under these conditions AgBrClI cubic microcrystals can be obtained with a reasonably uniform size at pAg 7.8. In the case of AgBrClI core/shell emulsions[3], which have a wide application in the photographic materials and technology by offering many advantages such as reletively high resolving power, high fog stability, and high blackening density.

MATERIALS AND METHODS

Materials. Gelatin was purchased from Sanofi Bio-Industries Co., Ltd., France. KBr, NaCl, KI and ammonia solution were purchased from Junsei Chemical Co., Ltd., Japan. $AgNO_3$(purity 99.8%) was purchased from You-chang Industries, Korea.

I. Preparation of common regular grains[4] with cubic Microcrystals. solution(A): 350 mL of 3.5% phenylcarbarmyl gelatin solution at 40°C. solution(B): 450 mL of aqueous solution containing 0.29 mol $AgNO_3$ and 45 mL, 30% NH_4OH. solution(C): 180 mL of aqueous solution containing 0.28 mol KBr, 0.12 mol NaCl and 0.006 mol KI. To a stirred solution(A) of 350 mL at pH 5.8 and 40°C were added solution(B) and solution(C) by means of a controlled double jet method maintaining pAg 7.8 for 30 sec. $AgBr_{0.69}Cl_{0.30}I_{0.01}$ cubic microcrystals were obtained after ripening 20 min as shown in Fig. 1.

II. Preparation of heterojunction type grains with cubic microcrystals. Solution(A): 350 mL of 3.5% phenylcarbarmyl gelatin solution at 40°C. Solution(B_1) : 350 mL of aqueous solution containing 0.12 mol $AgNO_3$ and 18 mL 30% NH_4OH. Solution(B_2): 270 mL of aqueous solution containing 17 mol $AgNO_3$ and 27 mL, 30% NH_4OH. solution(C_1): 70 mL of aqueous solution containing 0.1 mol KBr, 0.05 mol NaCl and 0.006 mol KI. solution(C_2): 110 mL of aqueous solution containing 0.18 mol KBr and 0.07 mol NaCl. To a stirred solution(A) of 350 mL at pH 5.8 and 40°C were added solution(B_1) and solution(C_1) by means of a controlled double jet method maintaining pAg 7.8 for 30 sec. $AgBr_{0.64}Cl_{0.32}I_{0.04}$ cubic microcrystals what are called "seed core" were obtained after ripening 10 min as shown in Fig. 2. To a prepared "seed core" emulsion at 40°C were added solution(B_2) and solution(C_2) in the same method. Finally, $AgBr_{0.69}Cl_{0.30}I_{0.01}$ cubic microcrystals, the so-called "heterojunction type grains(core/shell)", were obtained as shown in Fig. 3.

III. Sensitization of photographic emulsions with cubic grains. The emulsions obtained from cubic grains were chemically sensitized by adding S+Au[5]. Thus, the emulsions were ripened for 60 min at 50 °C after the addition of $Na_2S_2O_3$, 1.8×10^{-4} mol/Ag mol and AuSCN 10^{-5} mol/Ag mol.

RESULTS AND DISCUSSION

Figs. 1, 2 and 3 show homogeneous cubic microcrystals prepared by double jet method. The average size of the

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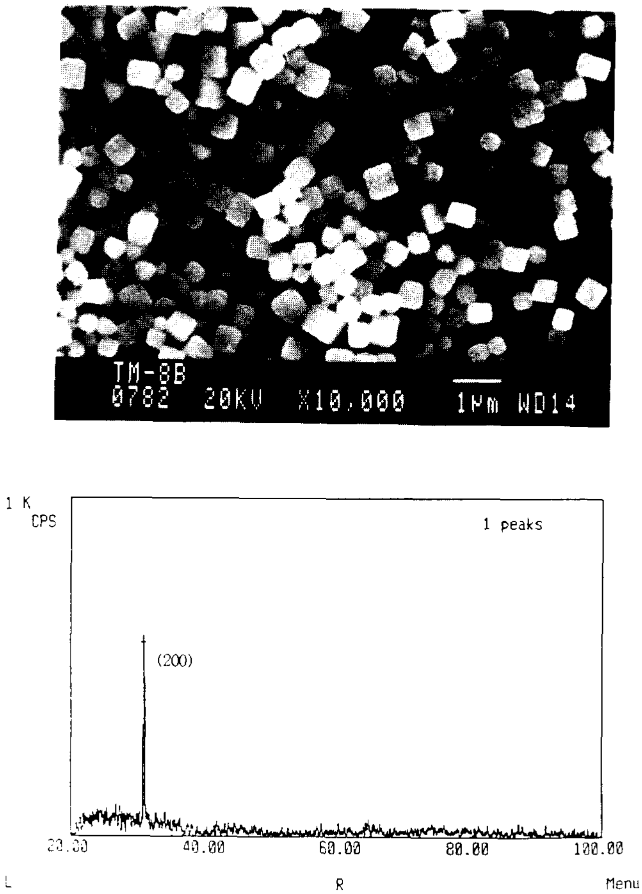

Figure1. The common regular grains with cubic microcrystals prepared by double jet method.

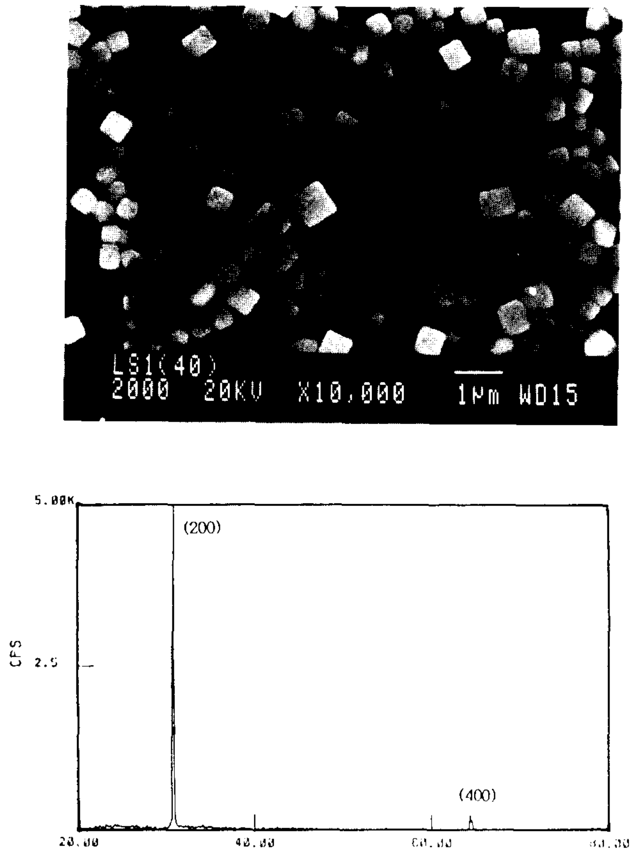

Figure 3. The "core/shell" grains of heterojunction type with cubicmicrocrystals.

Figure 2. The "seed core" grains with cubic microcrystals prepared by double jet method.

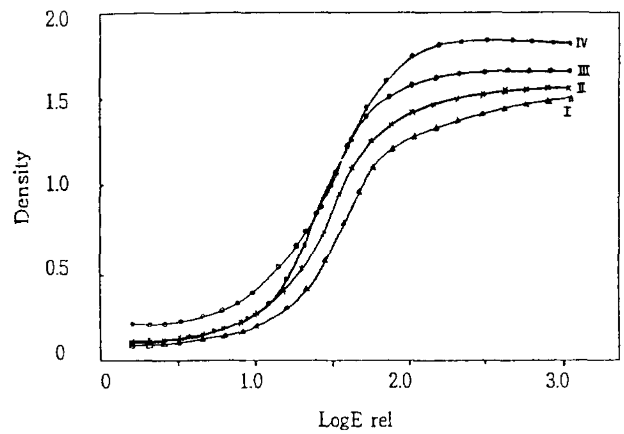

Figure 4. The photosensitivity of regular grain and heterojunction type grain according to iodide distribution with cubic microcrystals.

I. The emulsion of regular cubic grains ($AgBr_{0.69}Cl_{0.30}I_{0.01}$).
II. The emulsion of core/shell cubic grains ($AgBr_{0.69}Cl_{0.30}I_{0.01}$).
III. The emulsion of core/shell cubic grains ($AgBr_{0.68}Cl_{0.30}I_{0.02}$).
IV. The emulsion of core/shell cubic grains ($AgBr_{0.67}Cl_{0.30}I_{0.03}$)

AgBrClI cubic microcrystals was about 0.5 μm and the crystal habit[6] obtained from XRD was {200} as shown in Fig. 1 and Fig. 3. And the average size of the $AgBr_{0.64}Cl_{0.32}I_{0.04}$ cubic microcrystal "seed core" was about 0.35 μm as shown in Fig. 2. Fig. 4 shows the change of the photosensitivity of regular grain and heterojunction type grain according to iodide distribution in cubic microcrystal.

That is, after the chemical ripening by the addition of AuSCN and $Na_2S_2O_3$, higher photosensitivity was obtained from emulsion with heterojunction type cubic microcrystals. Especially, iodide content of 2.0 mol% which provides the optimum sensitivity was found. The structure failure grows with the increase of iodide content in AgBrClI phase. It is possible to suppose that the iodide content higher than 2 mol% provides structural imperfections. The influence on the photographic characteristics of heterojunction type "core/shell" grains offers us many advantages manufacturing the photographic materials.

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