

Study on Characteristics of Nanometer-sized Silver Iodobromide Emulsion*

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Introduction

Ever since C.R.Berry[1-2] found quantum size effect on nanometer-sized AgX grain and made studies on its anomalous absorption behaviour, much effort has been made on different aspects of nanometer-sized grain emulsion. H.Thiry,[3] M.Iwasaki and his coworkers[4] prepared nanometer-sized AgBr or AgBrI grain emulsion below 30nm scale and made some attempts on spectral sensitization; Investigated the mixture of AgBr and AgI emulsion with nanometer scale grains, T.S.Petrova[5] found photographic speed of the mixture was optimum at 2mol% to 4mol% of AgI; K.P.Johanson[6] studied the static and dynamic emission of nanometer-sized AgBr grain prepared in AOT reverse micelle. In our earlier work,[7] AgBrI grains between 13 and 30 nm of diameter were prepared by complexing precipitation and the mechanism of silver filament growth in development was also discussed. In the present study, attention was focused on the study of stability and sulfur sensitization of AgBrI emulsion with nanometer-sized grains.

Experiment

(I) Preparation of Emulsion

Three AgBrI emulsions were prepared by double-jet method.

(1) Emulsion 1 made at the Co-presence of Gelatin and PVA(polyvinyl alcohol)

Under moderate stirring, 30ml of 1.06mol.L^{-1} $AgNO_3$ solution and a mixture of 28.5ml of 1.06 mol.L^{-1} KBr solution and 1.5 ml of 1.06mol.L^{-1} KI solution were simultaneously added into a solution which consisted of 2g PVA, 6g gelatin and 240ml H_2O at the same rate of 15ml.min^{-1}. The precipitation procedure lasted 5 minute at 37°C, then a pre-made gelatin solution of 20g gelatin and 70ml H_2O was added under slow stirring to make sure the emulsion was homogeneous. Then the emulsion was stored up below 5°C.

(2) Emulsion 2 made at the absence of PVA

The operation was the same as that of emulsion 1 except that no PVA was used. The ratio of gelatin amount to silver content in Emulsion 1 and 2 was the same, i.e., 7.58 to 1.

(3) Emulsion 3 made with Lower Silver Content

The operation was the same as that of Emulsion 1, but the concerntrations of both $AgNO_3$ solution and KX(X=Br,I) solution dropped down to 0.71mol.L^1 to make the ratio of gelatin amount to silver content as 11.36 to 1. No PVA was used in this emulsion.

(II) Stability of Nanometer-sized Grain Emulsion

Take proper amount of Emulsion 1, 2 and 3 respectively in three beakers for physical ripening under various conditions. Make TEM photographs of the samples to observe the stabilization of PVA and gelatin on the grains in emulsion.

(III) Sulfur Sensitization

$Na_2S_2O_3$ solution was added as sulfur sensitizer into Emulsion 1 during chemical ripening. The influence of some experimental factors, including $Na_2S_2O_3$ amount added, sensitizing temperature, PH and PBr, on the speed during sulfur sensitization was studied.

Results and Discussion

(I) Stability of Nanometer-sized Grain Emulsion

Statistical analysis of grain size in TEM photo-graphs gave the average diameters listed in Table 1.

The data in Table 1 showed that the average diameters of the grains for both Emulsion 1 and 2 just after emulsification were 22.0nm and 19.1nm respectively in the case of the same ratio of gelatin amount to silver content. However, a little bit difference between both diameters was greatly expanded due to physical ripening. At the presence of PVA(Emulsion 1), no growth occurred after physical ripening for 30 min at 60°C, but at the absence of PVA(Emulsion 2), average diameter increased from 19.1nm to 23.8nm after physical ripening for only 5 min at the same temperature. The prolongation of ripening up to 15 min caused further increase of average diameter to 29.8 nm even if ripening temperature was only 40°C. These results indicated that the presence or absence of PVA in emulsification step had no obvious effect on grain size. During emulsification the ratio of gelatin amount to silver content for both Emulsion 1 and 2 (1.75:1) was enough to make absorption of gelatin on AgX grains saturated,[8] thus grain size was wholly dependent on the nucleation process and growth mechanics and was almost irrelative to PVA.

But it is possible that frequent collisions between AgX grains in the process of physical ripening make only gelatin unable to prevent coalescence or growth. In this case, the co-protection of PVA and gelatin on grains can effectively restrain the coalescence and growth. As the ratio of gelatin amount to silver content in emulsion increased from 7.58:1(Emulsion 2) to 11.36:1 (Emulsion 3), grain growth differed greatly for both emulsions after physical ripening at 40°C. i.e.,from 19.1nm to 29.8nm, a significant rise for Emulsion 2 and from 21.6nm to 22.8nm, an almost negligible one for Emulsion 3 even the ripening period for the latter was twice as that for the former. The stability of AgX grains in Emulsion 3 was obviously higher than that in Emulsion 2, which meant gelatin restrained efficiently the grain growth only in the case of lower silver content in emulsion. It implied that there should be a critical ratio of gelatin amount to silver content for the stability of emulsion with nanometer-sized grains at the presence of only gelatin as silver halide carrier. Above this ratio, the grains are stable, on the contrary, they grow up.

(II) Sulfur Sensitization of Nanometer-sized Grain Emulsion

The emulsion speed after sulfur sensitization was relevant to a list of experimental conditions including sensitizer amount, sensitizing temperature,pH and pBr, as shown in Figure 1 to Figure 4.

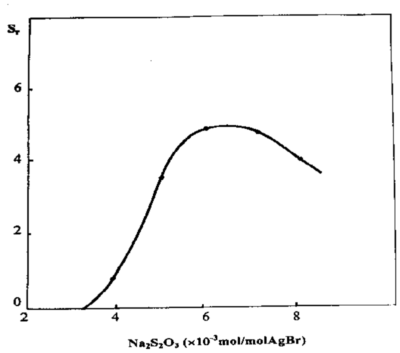

Figure 1: variation of speed with $Na_2S_2O_3$ amount, the sensitization period was 30 minute at 55°C.

Figure 4: variation of speed with PBr, the amount of sulfur sensitizer added was 4.0 x 10^{-3}mol $Na_2S_2O_3$/mol AgBr and sensitization period was 30 minute at 55°C. Figure 1 shows an optimum amount of sulfur sensitizer added in emulsion, i.e., 6 x 10^{-3} mol $Na_2S_2O_3$ per mol AgBr, at which emulsion speed was the highest in the present experiment. In this case, the quantities of Ag_2S specks produced by $Na_2S_2O_3$ on the grain surface may be of advantage for the formation of concentrated latent images. If Ag_2S is excessively or short formed, it may unfavourably affect latent images to lead to decrease of emulsion speed just as Figure 1 shows.

In sulfur sensitization of nanometer-sized grain emulsion, temperature was an important parameter influenced emulsion speed. Speed increased sharply when temperature rose from 50°C to 60°C. Experiments demonstrated that speed did not increase even if sulfur sensitization lasted 120 minute at 50°C while addition amount of $Na_2S_2O_3$ was 6.4 x 10^{-2} mol per mol AgBr. on the contrary, speed increased greatly while the sensitizing temperature reached 60°C despite addition amount of $Na_2S_2O_3$ was reduced to 4 x 10^{-3} mol per mol AgBr and sensitizing period was shortened to 30 minute, as shown in Figure 2.

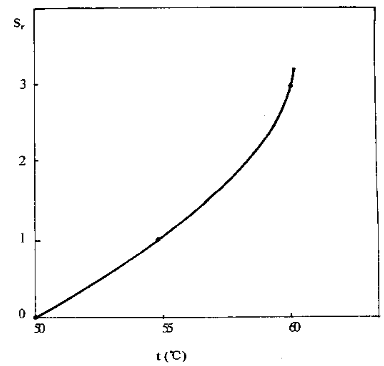

Figure 2: variation of speed with ripening temperature, the amount of sulfur sensitizer added was 4.0 x 10^{-3} mol $Na_2S_2O_3$/mol AgBr and sensitization period was 30 minute.

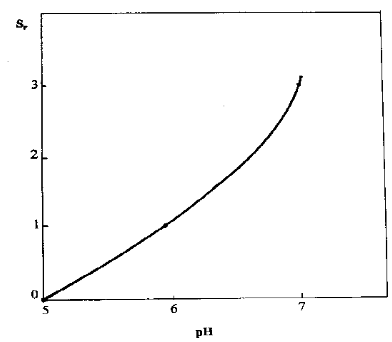

Figure 3: variation of speed with PH, the amount of sulfur sensitizer added was 4.0 × 10^{-3} mol $Na_2S_2O_3$/mol AgBr and sensitization period was 30 minute at 55°C.

In sulfur sensitization speed increased as pH rose, as shown in Figure 3. According to equilibriums through which $(Ag_2S)_n$ formed, rise of pH gave much convenience to the formation of $(Ag_2S)_n$ specks, consequently emulsion speed increased. It differed from the situation of general emulsion whose speed increased as pH decreased.[9]

In Figure 4, the dependence of emulsion speed on pBr in sulfur sensitization exhibited that the optimum speed occurred at pBr=5. Emulsion speed decreased when pBr was greater or less than 5. It will be seen from this that a proper pBr value was necessary for sulfur sensitization of nanometer-sized grain emulsion.

In summary, it is important to control addition amount of sulfur sensitizer , temperature, pH and pBr at the stage of chemical ripening for obtaining proper sensitization characteristics of nanometer-sized grain emulsion.

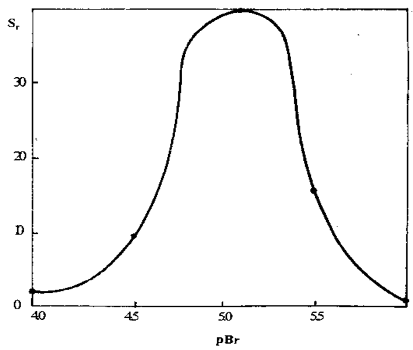

Figure 4: variation of speed with PBr, the amount of sulfur sensitizer added was 4.0 x 10^{-3} mol $Na_2S_2O_3$/mol AgBr and sensitization period was 30 minute at 55°C.

Appendix:

Table 1 Average Diameters ($\bar{d}$) of Grains in Emulsion

Emulsion type	Just emulsification (no ripening)	After physical ripening		After chemical ripening
	$\bar{d}$ (nm)	Ripening condition	$\bar{d}$ (nm)	$\bar{d}$ (nm)
Emulsion 1	22.0	at 60°C for 30mn	22.0	21.3*
Emulsion 2	19.1	at 40°C for 15min	29.8	
		at 60°C for 5 min	23.8	
Emulsion 3	21.6	at 40°C for 30 min	22.8	

*The condition of chemical ripening is following, addition of 4 x 10^{-3} mol $Na_2S_2O_3$ per AgBr at pH=7.0 and T=55°C for 30 minute.

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