Study on Characteristics of Nanometer-sized Silver Iodobromide Emulsion*

Xingpin Cui, Suwen Liu, Jun Yue
Department of Applied Chemistry, University of Science and Technology of China
Hefei, Anhui, 230026, P.R.China

Introduction
Ever since C.R.Berry1-2 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 coworkers4 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.Petrova5 found photographic speed of the mixture was optimum at 2mol% to 4mol% of AgI; K.P.Johanson6 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 AgNO₃ 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 H₂O 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 H₂O 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 concentrations of both AgNO₃ 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
Na₂S₂O₃ solution was added as sulfur sensitizer into Emulsion 1 during chemical ripening. The influence of some experimental factors, including Na₂S₂O₃ 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, 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$_2$S$_2$O$_3$ amount, the sensitization period was 30 minute at 55°C.](image1)

![Figure 2: variation of speed with ripening temperature, the amount of sulfur sensitizer added was $4.0 \times 10^{-3}$ mol Na$_2$S$_2$O$_3$/mol AgBr and sensitization period was 30 minute.](image2)

![Figure 3: variation of speed with PH, the amount of sulfur sensitizer added was $4.0 \times 10^{-3}$ mol Na$_2$S$_2$O$_3$/mol AgBr and sensitization period was 30 minute at 55°C.](image3)

![Figure 4: variation of speed with PBr, the amount of sulfur sensitizer added was $4.0 \times 10^{-3}$ mol Na$_2$S$_2$O$_3$/mol AgBr and sensitization period was 30 minute at 55°C.](image4)

In sulfur sensitization speed increased as pH rose, as shown in Figure 3. According to equilibriums through which (Ag$_2$S)$_n$ formed, rise of pH gave much convenience to the formation of (Ag$_2$S)$_n$ specks, consequently emulsion speed increased. It differed from the situation of general emulsion whose speed increased as pH decreased. 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.
Appendix:

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

<table>
<thead>
<tr>
<th>Emulsion type</th>
<th>Just emulsification (no ripening)</th>
<th>After physical ripening</th>
<th>After chemical ripening</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{d}$ (nm)</td>
<td>Ripening condition</td>
<td>$\bar{d}$ (nm)</td>
</tr>
<tr>
<td>Emulsion 1</td>
<td>22.0</td>
<td>at 60°C for 30min</td>
<td>22.0</td>
</tr>
<tr>
<td>Emulsion 2</td>
<td>19.1</td>
<td>at 40°C for 15min</td>
<td>29.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>at 60°C for 5min</td>
<td>23.8</td>
</tr>
<tr>
<td>Emulsion 3</td>
<td>21.6</td>
<td>at 40°C for 30min</td>
<td>22.8</td>
</tr>
</tbody>
</table>

*The condition of chemical ripening is following, addition of $4 \times 10^{-3}$ mol Na$_2$S$_2$O$_3$/mol AgBr at pH=7.0 and T=55°C for 30 minute.

References

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