# Preparation and Quantum Size Effect of Nanometer-sized AgBr/I Photographic Emulsion

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## Introduction

As we all know, the ultra-fine grain silver halide emulsion has played an important role in holography. The preparation for this kind of emulsions may be traced back to Lippmann emulsions about one hundred years ago[1]. The Crawford method published in 1954[2] was one of the improved methods afterward. The mean size is about 50nm usually. The character of the preparation for this kind of emulsion may be summarized as follows: low concentration of silver nitrate and potassium bromide, high proportion of gelatin and lower temperature in reaction.

In order to achieve ultra-fine AgBr grains, these three factors have to be involved in common methods. However, the preparation of the usual emulsion requires practically high concentration of silver nitrate which is in conflict with the requirement of low concentration in order to obtain ultra-fine grains. The unstable thermodynamic properties of nanometer-sized grains lead to their aggregation and growth. Therefore, it's difficult to obtain nanometer-sized silver halide emulsion with high concentration by usual methods.

In this paper, the nanometer-sized silver halide photographic emulsions which contained higher silver content were prepared by homogenous complex reaction in lower reaction temperature and strong viscosity of solution. The average grain sizes of the emulsions are 14nm-30nm. The ultra-fine development was also studied by TEM, and the nanometer-sized silver particles were reduced from ultra-fine silver bromide crystals by chemical reduction. The change laid the foundation of realizing ultra-high resolution.

## Experimental

### 1. Preparation of nanometer-sized AgBr/I emulsions

| | | | | |
|---|---|---|---|---|
| Solution A | 5g gelatin | 0.037mol EDTA | 0.037mol $AgNO_3$ | PH=10.5 40°C |
| Solution B | 5g gelatin | 0.037mol $Cd(NO)_3$ | 0.037mol KBr(I) | PH=2.5 40°C |
| Solution A | 40°C–24°C | double jets | coated cooled | washed dried |
| Solution B | 40°C– | 7min | | 0-5°C |

Solution A consisted of 5 percent gelatin and 0.37mol/L $[AgEDTA]^-$ complex ions which were made with $AgNO_3$ and editic acid. The PH value was adjusted to 10.5 at 40°C with NaOH solution. Solution B was 5 percent deionized bone gelatin also and 0.37 mol/L $[CdBr]^+$ complex ions which were made with $Cd(NO_3)_2$ and KBr solutions. The PH value of the solution was adjusted to 2.5 at 40°C with $HNO_3$.

To a reaction vessel equipped with a stirrer were simultaneously added 100ml of solution A and 100ml of Solution B at 24°C . The solution also contained 0.7ml antifoaming agent. After being stirred for 7min at 24°C , the emulsion was then coated, cooled, washed in running water and dried at 25°C.

### 2. Ultra-fine development

The specimen was developed by P-phenylenediamine developer at 20°C, fixed by F-11 fixer for 8min, and washed for 15min.

### 3. Determination

The size and shape of nano-grains were examined by means of transmission electronic microscope (TEM) and X-ray diffraction. The specimen for X-ray diffraction is the emulsion film without base, and the size is 1.5cm×1.5cm.

## Results And Discussion

### 1. Monodispersity

The precipitation of AgX can be given as following formula

$$[AgEDTA]^- + [CdX]^+ = AgX \downarrow + CdEDTA \qquad (1)$$

compared with the usual method, the method described above for fabricating an ultra-fine silver halide emulsion has three advantages at least. First, the 0.37mol/L solutions have so low a condensation point that they can keep good flowability at a temperature as low as 24°C ( while the usual emulsion will condense about at 37°C). Obviously lower temperature keeps the particles from Ostwald Ripening efficiently. Second, it's well known that the rate of a complex reaction depends upon the molecular structure of complexes. For a chelate compound, $[AgEDTA]^-$, the rate of substitution reaction is slower than that for a common

compound. Therefore the reactants have been mixed fully before they react thoroughly, and in the mixture the supersaturation of silver halide changed very little because it was controlled by the rate of substitution reaction. The result of calculation is as follows:

| The solubility product (25°C) | with complex compounds | without complexes |
|---|---|---|
| Ksp(AgBr)= $5.0\times10^{-13}$ | 0.37mol/L $[AgEDTA]^-$ and $[CdBr]^+$ $[Ag^+][Br^-]=1.39\times10^{-4}$ | 0.37mol/L $AgNO_3$ and KBr $[Ag^+][Br^-]=0.37\times0.37$ |

It shows that low $[Ag^+]$ and low $[Br^-]$ are favorable to prepare ultra-fine monodispersing grains. Third, as a dispersing medium the gelatin, in the reaction agents is also important to this kind of emulsion, it reduces the rate of reaction and keeps the solution higher viscosity and smaller diffusivity. According to the theory of crystal growth and homogerous nucleation, the dispersion degree (q) may be written as:

$$q = \frac{\Delta C^m \cdot \eta \cdot \delta}{C_0^{m'+1} \cdot D} \qquad (2)$$

where $\Delta C$ is the supersaturation concentration, $C_o$ is the solubility of the grain and $\eta$, media viscosity, $\delta$, the thickness of double electric layers, D, the diffusivity, m and m' are contants.

**2. Grain-size of silver halide**

The particles average sizes were determined from the X-ray line width using Scherrer's equation[3] (Equation 3).

$$D=K\lambda/\sqrt{B^2-b^2\cos\theta} \qquad (3)$$

**Table 1 The average size of silver halide particles**

| Simple | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $x_1$/% | 0 | 4 | 8 | 11 | 16 | 20 |
| d/nm | 30 | 25 | 20 | 18 | 16 | 20 |

Table 1 presents the average grain size of emulsion from 1 to 6. The data show that the size of grains closely relates to the iodide content, i.e. the particle size gradually decrease s with the increasing of iodide content, however, it begins to enhance after the iodide content is up to 11 percent. According to Berry[4], AgI would be precipitated only at the beginning of the precipitation, and serve as nuclei. The enhancement of nuclei numbers with addition of iodide leads to particle sizes decreasing. After the nuclei are up to saturation, the grain size begin to increase.

3.Quantum size effect

The emulsion containing 11% iodide was chosen for measurement of UV-Visible absorption because of the smallest mean size among the six emulsions . From the initial to the end of the preparation, the reaction system was traced and measured by UV-Visible absorption method, i.e. the change was measured dynamically. It is observed that the threshold value of absorption spectrum at long wavelength shifts toward longer wavelength when the reaction time is prolonged. As the complexing reaction continues and the Ostwald ripening begins, this red shift should result from gradual growth of the silver halide particles. In other words, the threshold value of absorption spectrum at long wavelength shifts toward shorter wavelength because the size of particles decreases in the emulsion. As we know, in the solid state silver halides, the quantum energy corresponding to long wavelength edge in absorption band characterizes a minimum energy of electron transition from solid surface to vacuum, including indirect transition of exciton[5].

Exciton is electron-hole pair which depends upon Coulomb Forces. This electron-hole interaction has to be included for a more quantitative treatment of the quantum size effect. By assuming the energy band parabolic near the bandgap (the effective mass approximation), the size-dependent shift in the exciton energy of a nanometer-sized particle can be derived as[6,7]

$$\Delta E = \frac{h^2}{8R^2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) \qquad (4)$$

where R is the particle radius and $m_e$ and $m_h$ are the electron and hole effective mass, respectively. $\Delta E$ is the particle-in-a-box energy in fact. Equation 4 bases on effective mass approximation and the spatial correlation effect is omitted. Equation 4 containing the basic physics of quantum size effect can be expected to explain "blue shift" phenomena for nanocrystal qualitatively.

In order to find out the relation between particle size and the wavelength of absorption spectrum, the data which were measured dymatically in UV-Visible absorption were analyzed further. We pick out the wavelength at the edge of half intensity width in absorption spectrum, and compare it with the reaction time. Table 2 shows the relation between the wavelength and the time.

**Table 2. The relation between the wavelenth at edge of half intensity width and growing time of particles**

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| λ/nm | 444 | 488 | 505 | 524 | 538 | 552 | 568 | 578 | 588 |
| t/s | 7 | 85 | 163 | 319 | 475 | 709 | 1021 | 1411 | 1875 |

When the data in Table 2 were dealt with the method of linear regression, we found that the relation among wavelength, the time and the particle's radius can be written as

$$\lambda = A e^{Bt} \tag{5}$$

$$R = A' e^{B't} \sqrt{\frac{1}{m_e} + \frac{1}{m_h}} \tag{6}$$

where A and B are experimental constants, and their values are $4 \times 10^{-7}$ and $3.7 \times 10^{-2}$, respectively. When the light radiant energy ($Nh\nu$) vs the absorption of red shift was considered, the relation between the particle's radius and reaction time can be reflected by equation 6. In equation 6, A' and B' are constants. The equation can be expected to show the particle's growth vs. time qualitatively.

Finally we should point out that although the process of the particles' formation can not be measured at the first few seconds because of the equipment itself, it is still a simple method to study nanometer-sized silver halide emulsion dynamically.

## Conclusions

The nanometer-sized silver halides photographic emulsion which contains more silver can be prepared by homogenous complex precipitation. The particles' size in the emulsion relates close with the iodide content. In UV-visible absorption spectrum, the wavelength at the long wavelength shifts to longer wavelength vs. the growth of the particles. the relation between the particle size, the growth time of crystal and the wavelength at the edge of the long wave direction can be given approximately.

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