Preparation and Study of Ultra-Fine Particle Silver Halide in Fish Gelatin Medium as Protective Colloid *

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Abstract

Components of fish gelatin protein are examined to show dominant α component and the lack of γ component in it ,which is different from general bone gelatin. By fish gelatin acting as protective colloid, ultra-fine particles AgBrI with average size from 14.3nm to 14.6nm are prepared successfully in the case of the ratio of gelatin amount to silver content as 6:1, 4:1, 3:1, respectively. After emulsion ripening, the coalescence and growth of particles are not discovered except of the emulsion with gelatin / silver ratio as 3:1 by means of TEM observation. It means that the ultra-fine AgBrI particles in fish gelatin protective medium possess satisfactory thermostability when gelatin /silver ratio is in excess of 3:1. The efficacy of chemical sensitization of the ultra-fine particle AgBrI emulsion depends on sensitizing conditions. In the case of sulfur plus gold sensitization, suitable increase of sensitizer amount and appropriate prolongation of chemical ripening period are favorable for high sensitivity, but fog density does not raise.

Introduction

Gelatin is made mostly from calf and pork skins or bones. The favorable physical, chemical and photographic properties caused gelatin to remain the dominating vehicle for silver halide for more than a century. Fish gelatin is extracted from the skin of deep cold water fish such as cod, haddock and pollack. It consists of some kinds of long chains of amphoteric amino-acid molecules with a molecular weight of 30,000-60,000 daltons. Its water solution do not gel at room temperature (25°C) which allows for applications not possible with animal gelatin. Application of fish gelatin in the manufacturing process of silver halide emulsion can offer a way to control size, size distribution and shape of the particles. M. Tomoo reported[1] that a silver halide emulsion, whose average grain size is below 0.1μm, contains at least one kind of fish gelatin as protective colloid which is used in the manufacturing process. However, it is difficult to make the ultra-fine particle, i.e. nanometer-sized one, AgBrI emulsion with high silver amount and thermostability in the case of only animal gelatin as protective colloid. In the present study, protein components of fish gelatin were characterized by determination of distribution of its protein with respect to molecular weight, firstly. A future exploration of nanometer-sized particles AgBrI emulsion making in only fish gelatin medium as protective colloid and chemical sensitization of this nano-particle emulsion was performed.

Experiment

1. The source of fish gelatin

Fish gelatin used in the experiment is provided by Norland Products Inc., US. Norland fish gelatin is manufactured by the hydrolysis of collagen, which is the principle protein found in skin and bone. Fish gelatin is a Type A gelatin (acid extracted).

2. Distribution determination of fish gelatin proteins with respect to molecular weight

Distribution of fish gelatin proteins with respect to molecular weight were determined by SDS-PAGE method[2]. At first, 1ml of 2% solutions of the acid-soluble

collagen, the fish gelatin and the inert bone gelatin were taken into the vessels with 4ml of the test solution for SDS-PAGE respectively. After being heated at 100°C for 3-5minutes and subsequently cooled to room temperature, the separations of these mixed solution were made by SDS-PAGE. Lastly distribution information of gelatin proteins were calculated according to the results from the SDS-PAGE scanning chromatograms.

3. Preparation and TEM observation of ultra-fine AgBrI particles in fish gelatin medium as protective colloid

0.8mol/L $AgNO_3$ water solution and a mixed water solution of 0.76mol/L KBr and 0.04mol/L KI were simultaneously added into 5%(wt.) of fish gelatin water solution at 30°C under appropriate rate of agitation by a double-jet technique. The process of emulsification and physical ripening was performed for 10 minutes. At the end of physical ripening , supplementary fish gelatin was added to keep 5%(wt.) of fish gelatin concentration in the emulsion. In the final emulsion , the ratio of fish gelatin amount to silver content (gelatin / silver ratio) was about 4:1. As above-mentioned method, the emulsions with gelatin /silver ratio as 6:1 and 3:1 were prepared by adjusting jetting amounts of $AgNO_3$, KBr and KI solution, respectively. The three emulsions' samples diluted were spotted on copper grids respectively for TEM observation of particles size. In the present observation, a set of HATCH-800 type Transmission Electron Microscope was utilized.

4. Chemical sensitizing experiment of ultra-fine particle AgBrI emulsion containing fish gelatin

The aforementioned emulsion with gelatin / silver ratio as 4:1 was flocculated at pH=3~4 for 30 minutes, then washed by de-ionized water at 3-4°C to remove soluble salts. With a pH adjustment, the granular precipitate was redispersed to reconstitute emulsion at 30°C which was diluted by de-ionized water to achieve a 7.5%(wt.) of gelatin water solution. Added certain amount of sulfur sensitizer or sulfur plus gold sensitizer, the emulsions were ripened for different periods at 55°C then uniformly coated on a film base and air-dried for several hours. The coated sheets were exposed for ten minutes at color temperature 5500K. The exposed sheets were developed in D-72 developer solution for fifteen minutes and fully fixed in F-5 fixing solution at 18°C, then washed and dried. The density values measured successively were input to a microcomputer to calculate photo-sensitivity data, including relative sensitivity (Sr) ,fog (D_0).

Results

1. According to the distribution figure of fish gelatin protein with respect to molecular weight, the data of relative contents of protein components in fish gelatin was shown in Table 1. The data of an inert bone gelatin was also shown in Table 1.

Table 1. Relative Contents of Protein Components (%)

samples	α_1	α_2	$\alpha_1+\alpha_2$	α_1/α_2	β	γ
fish gelatin	13.3	54.3	67.6	0.25	32.4	—
bone gelatin	40,4	17.9	58.3	2.3	30.9	10.6

2. According to TEM pictures, the average particle sizes of a series of ultra-fine AgBrI particles with various ratio of fish gelatin amount to silver content were calculated statistically to list in Table 2.

Table 2. Average sizes($\bar{d}$) of ultra-fine AgBrI particles with various ratio of fish gelatin amount to silver content

Emul. NO.	ratio	$\bar{d}$ (nm)	σ
1	6:1	14.2	± 0.62
2	4:1	14.3	± 0.65
3	3:1	14.6	± 0.83

3. The data of sensitometric properties of ultra-fine particle AgBrI emulsion chemical-sensitized for different period at 55°C were listed in Table 3.

Discussion

The data in Table 1 showed that there are several significant characters in components of fish gelatin protein which are different from that of inert bone gelatin used generally in photographic emulsion, i.e., there hardly exists γ component with high molecular weight and the part of lower molecular weight dominantly concentrates on α component. α component is a long

Table 3. Sensitometric properties of ultra-fine particle AgBrI emulsion chemical-sensitized

Chemical sensitizer	ripening time (min.)	S_R	D_0 (fog+base)
1	30	—	0.02
	60	1	0.02
2	30	2	0.02
	60	5	0.02
3	30	5	0.02
	60	19	0.02
4	30	9	0.02
	60	33	0.02

Note:

1. 1.2ml 0.263%(wt.) $Na_2S_2O_3$ water solution
2. 1.5ml 0.263%(wt.) $Na_2S_2O_3$ water solution
3. 1.0ml 0.263%(wt.) $Na_2S_2O_3$ water solution and 1.2ml AuSCN water solution
4. 1.5ml 0.263%(wt.) $Na_2S_2O_3$ water solution and 1.5ml AuSCN water solution

single chain of helical structure with lower molecular weight than that of β and γ component. It allows to prepare photographic emulsion at lower temperature, which is favorable for the formation and stability of ultra-fine AgBrI particles. The special characters of low molecular weight and single chain of α component of fish gelatin possibly caused it to coat AgBrI particles more steadily and its amino acid residue to bind to silver on the surface of AgBrI particles more easily, so that particle growth may be hindered. Besides, the effect of α component on the sensitometric properties of those AgBrI particles may be more stronger than other components in gelatin. Tables 2 showed the result of TEM observation and statistical analysis. In this paper ,standard deviation (σ) was used to quantitatively assess the dispersion degree. The data in Table 2 showed that the average particle sizes ($\bar{d}$)of AgBrI emulsion No. 1,No. 2, No. 3 just after emulsifying and physical ripening for ten minutes whose ratio of fish gelatin amount to silver content were 6:1, 4:1 and 3:1 are 14.2, 14.3 and 14.6nm, respectively. Then standard deviations (σ) are 0.62, 0.65, 0.83, respectively. It is worthy to note that the average sizes have a bit of variation from 14.3nm to 14.6nm, but standard deviations occur a rather large change from 0.65 to 0.83 as the silver content is increased in the case of gelatin / silver ratio from 4:1 to 3:1. By means of TEM observation, some of the particles of emulsion No. 3 grow up to above 18.0nm significantly so that the monodispersitivity of particles is destroyed. One may conclude that as the silver content is increased to 0.34g in 1g fish gelatin, the stability of AgBrI nano-particles decreases due to the diminution of the colloid protective power of gelatin. During emulsification the ratio of gelatin amount to silver content for Emulsion No.1, No. 2 and No. 3 was enough to make absorption of gelatin on AgX grains saturated[3], thus grain size was wholly dependent on the nucleation process and growth mechanics. The physical ripening itself is restrained by gelatin which would hinder coalescence or growth of nano-particles formed during emulsification. But when gelatin / silver ratio decreases to 3:1 fish gelatin is unable to fully hinder coalescence and growth of nano-particles so as to form some large grains.

The study on bone gelatin demonstrated that the gelatin with higher content of α_1 component and larger ratio value of α_1 to α_2 possessed stronger reducibility[4] which can be helpful to improve the photo-sensitivity[5]. The data in Table 1showed lower content of α_1 component and small ratio value of α_1 to α_2 in the fish gelatin. It can be unfavorable influence on the sensitivity of emulsion. The speeds and fogs of emulsion No. 2 after sulfur sensitization and sulfur plus gold sensitization were relevant to a list of experimental conditions including sensitizer amount and ripening times showed in Table 3. Owing to sensitometric properties of emulsion are relative to AgBrI particle growth, the sample of emulsion chemical-sensitized for 60 minutes was observed by TEM again. The result proved AgBrI particles do not grow up, so stability of those particles was excellent. For so small AgBrI particles, much more sensitizer was required than the general photographic emulsion. With increase of sensitizer amount and chemical ripening period relative sensitivity of emulsion raises, especially in the case of sulfur plus gold sensitization. It is interested that the fog (D_0) does not increase as those conditions change. In the previous study, it was observed that the prolongation of chemical ripening period of a general micrometer-scale

particle emulsion to which some of fish gelatin were added as the second-ripening supplementary gelatin led to sharp increase of fog density. It may be attributed to significant difference of grain size which may influence behaviors of photoelectron and interstitials in emulsion microcrystal, so as to be showed various photo-sensitometric properties. A further study is doing now.

Conclusion

α component is major and γ component is lack in fish gelatin which is different from that in general bone gelatin. Ultra-fine particles AgBrI of a better monodispersity and thermostability with average size of 14.3nm is prepared in the case of gelatin / silver as 4:1 by fish gelatin acting as protective colloid. The emulsion are chemical sensitized, along with appropriate chemical sensitizer amount increasing and appropriate chemical ripening period prolonging, the relative sensitivity raises, but the fog density does not raise.

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