Photosensitivity of Nanoparticle Silver Halide Dispersions in Fish Gelatin

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Abstract

A photographic emulsion, which consists of suspensions of silver iodobromide nanoparticles in fish gelatin, was made. The average size of the particles calculated based on XRD data was 16nm. The photosensitivity of nanoparticle emulsion layer was considerably relative to the wavelength (λ_{max}) of maximum radiant intensity on exposure. It was found that as change of λ_{max} from 525nm to 1010nm, the sensitivity (S) was increased by 1.5 times and gamma of the emulsion layer slightly decreased, which implies this nanoparticle AgBr/I emulsion being more sensitive to near infrared radiant. The microwave photoconductivity measurement showed that the electron lifetime in emulsion particles shortened obviously, indicating a mass of shallow traps on the nanoparticle surfaces. A higher ionic conductivity characterized by $\log f_{max}$, the logarithmic scale of experimental frequency at maximum value of dielectric loss, was observed by the means of dielectric loss test, which was considered as the formation of interstitial silver ions with high concentration on the surfaces of the nanoparticles. With controlling the amount of sulfur sensitizer and sensitization time, the effect of chemical sensitization on photosensitivity of the nanoparticle AgBr/I emulsion was also studied. The result showed that sensitivity and gamma increased with increase of both amount of sulfur sensitizer and sensitization time, but the excessive amount of sulfur sensitizer led to the occurrence of rapidly additive fog density. In the case of the optimum sensitivity and gamma, sulfur sensitization specks on the AgBr/I nanoparticle surface can be roughly estimated as 1-10.

Introduction

A very low initial photosensitivity of nanoparticle silver halide emulsion caused by weak intensity of scattered light and less silver content in it limits its application as photographic material. Searching a way to increase photosensitivity of nanoparticle silver halide emulsion is a research focus. The attempts to achieve high sensitivity by chemical sensitization were made and the results were various[1-4]. In the present study, the attention was concentrated on photosensitivity and photoelectron-ionic behavior of a nanoparticle AgBr/I emulsion sensitized by sulfur sensitizer. In the experiment, a special fish gelatin extracted from the skin of deep cold water fish was used as protective colloid medium to make the nanoparticles emulsion[5]. The low gelling temperature of the fish gelatin is of great advantage of decreasing the ratio of gelatin to silver, resulting in higher silver content in the emulsion.

Experiment

1.Emulsion preparation

Nanoparticle silver iodobromide emulsion with ratio of gelatin to silver as 5:1 and the iodine content as 5mol% was prepared in fish gelatin medium as protective colloid by double-jet technique at 30℃for 10min. Then XRD test for dried coating layer of the emulsion was performed.

2.The effect of spectral characteristics on photosensitivity of nanoparticle AgBr/I emulsion

In this paper, the wavelength (λ_{max}) of maximum radiant intensity was applied to characterize spectral property of light resource. After sulfur sensitization at 50℃for 45mins in the presence of $1.7*10^{-2}$mol $S_2O_3^{2-}$/mol AgBr, the emulsion was coated on a film base and air-dried for several hours, then exposed for 15mins on CGG sensitometer, λ_{max} of light resource is 525nm, 902nm, 1010nm, respectively.

3.Electric behavior measurement

The principles of measuring photoconductivity and ionic conductivity of emulsion grains have been reported previously[6].

The photoconductivity measurement: A strip of emulsion film, dried by blowing at room temperature, was put in the resonance cavity of a 35GHZ microwave photo-conductivity apparatus. The exposure of sample on the tuned microwave cavity to a light pulse created electronic charge carries, which could absorb the microwave energy and detune the microwave cavity to give the signal in proportion to the concentration of electronic charge carriers. It is considered that only free photoelectrons are usually responsive to the signal of microwave photoconductivity. The mean life (τ) of the electrons can be determined by the slope (k) of a plot of signal intensity vs. time, that is photoconductivity decay curve, i.e., τ =1/k. The maximum value (I_0)of signal is a measurement of the relative amount of photoelectrons generated by the exposure[7].

The ionic conductivity measurement: A dried emulsion film with a thickness of 100 µm was used to measure ionic conductivity by a TL-10 dielectric loss instrument at room temperature. The ionic conductivity of emulsion grains was determined by measuring the frequency (f) dependence of the dielectric loss (ε'') of emulsion layers. The logf value corresponding to maximum ε'' value, named $\log f_{max}$, was taken to be the relative ionic conductivity[7].

4.Sulfur sensitization

Sulfur sensitization was carried out by digesting the emulsion at 50℃for from 30mins to 60mins in the presence of sulfur sensitizer, the amount of which was from $4.33*10^{-3}$ mol $S_2O_3^{2-}$/mol AgBr to $43.36*10^{-3}$ mol $S_2O_3^{2-}$/mol AgBr.

5.Developing process and optical density measurement

The exposed emulsion sheet was developed in D-76 developer solution for 15mins, then completely fixed in F15 fixer solution. After the sheet being washed fully and dried, the optical density was measured on TD-504M densimeter, then corresponding data of photosensitivity was calculated.

Results and discussion

1.Size and thermostability of AgBrI nanoparticles

According to Shere's formula[8]:

$$D=K\lambda/\beta_0 COS\,\theta \quad (1)$$

where K=0.9, λ is wavelength of X-ray, β_0 is half- high length of spectral peak of XRD with radian as its unit, and θ is Bragg angle with degree as its unit, average size of particles was calculated on the basis of XRD data 16nm. A week later, size of particles has been tested again via XRD and the size change was negligible. It indicated that nanoparticle AgBr/I emulsion in fish gelatin medium possessed satisfactory thermostability, that is, fish gelatin efficiently controlled the size of particle and prevented it from coalescence and growth.

2.The effect of wavelength of maximum radiant intensity on photosensitivity of nanoparticle AgBr/I emulsion

Photosensitivity of nanoparticle AgBr/I emulsion was relative to spectral characteristics of light resource. The dried emulsion sheets were exposed by light source with various wavelength (λ_{max}) of maximum radiant intensity. The effect of λ_{max} on photosensitivity of nanoparticle emulsion was explored. The results obtained were shown in Fig1.

The figure showed that as change of λ_{max} from 525nm to 1010nm, sensitivity increased by 1.5 times and gamma decreased slightly, which implied this nanoparticle AgBr/I emulsion being more sensitive to near infrared radiant.

3.Electrical properties of nanoparticle silver halide

Photoconductivity: The kinetic curve of photoconductivity decay, drawn with signal intensities of photoconductivity vs. time, was shown in Fig2. The photoconductivity decay process obeys first-order kinetic rule. The mean electron lifetime (τ) of the nanoparticle silver halide was thus calculated as 13.75 µs based on the line slope (k), i.e., τ =1/k. Compared to some larger emulsion grains, of which τ values were in the range of 0.1μs to 3μs[9a], the electron lifetime in nanometer-sized AgBr/I emulsion particles shortened obviously. It was considered that if shallow traps are present, the electron will be repeatedly trapped and thermally released before it is permanently trapped, so that it spend part of its lifetime in the traps. Therefore, the shorter electron lifetime observed in the present study indicated the present of a mass of shallow traps on the nanoparticle surfaces, furthermore, emphasized the dominance of the nanoparticle in determining the electronic properties of the emulsion. This result supported the proportionality of electron life to grain size for unsensitized AgBr emulsion grains[10].

Ionic Conductivity: A curve of dielectric loss values (ε'') versus logarithmic scale of experimental frequencies for the nanoparticle AgBr/I emulsion was shown in Fig3. The logarithmic scale of the frequency at maximum dielectric loss ($\log f_{max}$) obtained from this curve was 6.1 f. It was reported that the conductivity of cubic AgBr emulsion grains was proportional to the surface to volume ratio of the grains, indicating that the charge carriers were created from the grain surface[11]. The large $\log f_{max}$ value of the AgBr/I nanoparticles, which reflected the high ionic conductivity, was caused by high ratio of the surface to volume in the nanoparticles. It was considered that the energy level of a silver ion at a surface site is higher than that of a silver ion at a lattice position. Interstitial silver ions with high concentration can be thus formed on the surfaces of the nanoparticle. The motion of these silver ions eventually led to high ionic conductivity in nanoparticle AgBr/I emulsion.

4.Sulfur sensitization of nanoparticle AgBr/I emulsion

It is well know that chemical sensitization is effective to improve photosensitivity of photographic emulsions. In this report, the influence of amount of sulfur sensitizer and sensitization time on sensitivities of nanoparticle AgBr/I emulsion was investigated. The results were shown in Fig4-5.

Fig4 showed that sensitivity of emulsion film increased quickly with the increase of the amount of sulfur sensitizer. As the amount of sulfur sensitizer was $2.6*10^{-2}$ mol $S_2O_3^{2-}$/mol AgBr, the sensitivity could be over 120 ASA for a longer exposure time (15mins), while corresponding fog density was below 0.08. When the amount of sulfur sensitizer was larger than $3.5*10^{-2}$mol $S_2O_3^{2-}$/mol AgBr, fog density increased rapidly which implied the formation of fog center. Gamma increased first and then decreased with sulfur sensitizer increasing. It is suggested that for the nanoparticle AgBr/I emulsion there exists an optimum added amount of sulfur sensitizer. Here the optimum amount was $2.6*10^{-2}$ mol $S_2O_3^{2-}$/molAgBr. It's generally believed that the formation of sulfur sensitization center is on the basis of two-step mechanism, i.e., formation of Ag_2S and rearrangement of Ag_2S into specks in which the second step is the rate-determining step[9b]. According to this view, the number of sulfur sensitization centers (i.e., Ag_2S centers) is closely relative to the amount of sulfur sensitizer used in sulfur sensitization. It is now accepted that sulfur sensitization centers are shallow electron traps, where latent image centers are preferably formed[9b]. Although electron-trapping sensitization centers enhance the nucleation process (i.e. formation of latent subimage centers), they disturb the growth process, decreasing the rate for a subsequent electron to reach the nucleus and increasing the probability for the subsequent free electron to take part in the formation of another competing nucleus. Therefore, number of sulfur sensitization centers as shallow electron traps formed during sulfur sensitization is important for efficient formation of latent image centers.

In the present experiment, in a certain range of sulfur-sensitizer amount, the photographic sensitivity of the emulsion layer enhanced as increasing the amount of sulfur sensitizer, which could be attributed to efficient formation of latent image centers. while the excessive amount of sulfur sensitizer was used, increase of probability for formation of a mass of competing nucleus (i.e. latent subimage centers) made fog density going up rapidly. For nanoparticle AgBr/I emulsion, optimization of the number and depth of shallow electron traps provided by sulfur sensitization center is also of great importance for efficient formation of latent image centers, which will be helpful to increase its photosensitivity. For the nanoparticle AgBr/I emulsion, in the case of optimum amount of sulfur sensitizer, the maximum number of Ag_2S molecules on a AgBr/I nanoparitcle surface was roughly estimated as 1000. According to Ref.12, the statistic numbers of silver sulfide molecules in a sulfur sensitization center were from 100 to

1000. So it was suggested that the number of sulfur sensitization center on a AgBr/I nanoparticle surface is from 1 to 10.

Fig5 showed that film sensitivity and gamma increased but fog density is little with the increase of sensitization time. Appropriate prolongation of time was favorable for reaction of sulfur sensitizer with Ag^+ to form silver sulfide and, especially, the arrangement and coalescence of silver sulfide into sulfur sensitization center. So that, high photosensitivity of nanoparticle silver halide emulsion can be reached.

Conclusion

A nanoparticle AgBr/I emulsion with average size of particle as 16nm was made in fish gelatin medium as protective colloid. It possessed satisfactory thermostability and lower ratio of gelatin to silver as 5:1. As increasing the wavelength (λ_{max}) of maximum radiant intensity of light source on exposure from 525nm to 1010nm, the sensitivity was enhanced by 1.5 times, which implied this nanoparticle AgBr/I emulsion being more sensitive to near infrared radiant. The electron lifetime in the nanometer-sized AgBr/I emulsion particles shortened obviously, indicating a mass of shallow traps on the particle surfaces. The larger $\log f_{max}$ value of the AgBr/I nanoparticle, which reflected higher ionic conductivity, was considered as the formation of interstitial silver ions with higher concentration on the surfaces of the nanoparticles. The sulfur sensitization was efficient to enhance photosensitivity of the nanoparticle AgBr/I emulsion. The increase of sulfur sensitizer amount was favorable for high sensitivity but the excessive amount of sulfur sensitizer resulted on fog density increasing rapidly. A optimum amount of sulfur sensitizer in the present study was suggested as $2.6*10^{-2}$ mol $S_2O_3^{2-}$/mol AgBr. With appropriate prolongation of sensitization time, the higher sensitivity of nanoparticle emulsion can be reached. Under a condition of optimum sulfur sensitization, the number of sensitization centers on a AgBr/I nanoparticle surface can be roughly estimated as from 1 to 1o.

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Appendix:

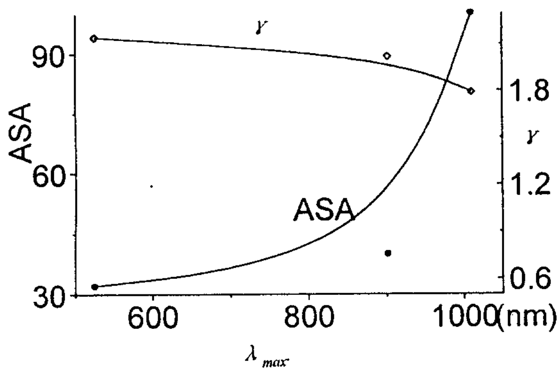

Fig1. Photosensitivity (ASA; ●) and gamma (γ ; ◇) as a function of λ_{max}

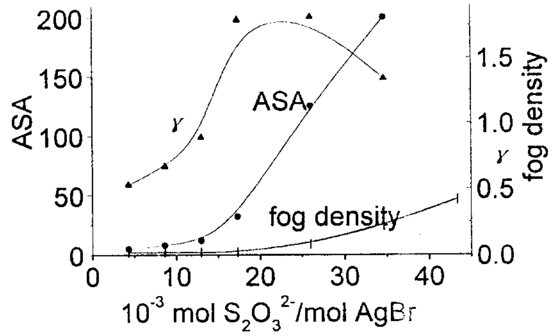

Fig4. Photosensitivity (ASA; ●), gamma (γ ; ▲) and fog density (|) as a function of the amount of $S_2O_3^{2-}$ used for sulfur sensitization.(λ_{max} of light source is 525nm)

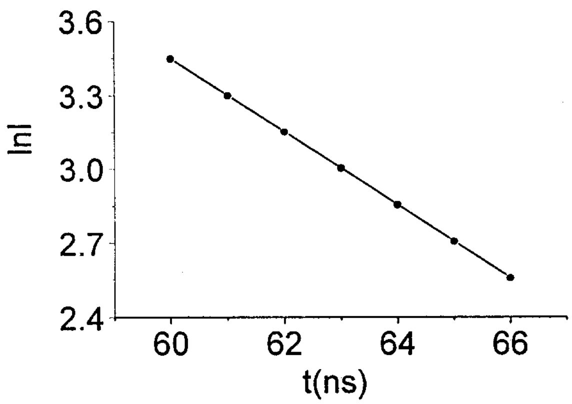

Fig2. A kinetic curve of photoconductivity decay, drawn with natural logarithm (lnI) scale of signal intensities of photoconductivity vs. time (ns).

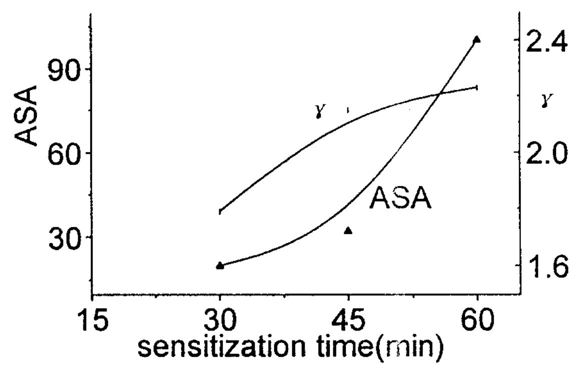

Fig5. Relation of photosensitivity (ASA; ▲) and gamma (γ ; |) to sensitization time. (λ_{max} of light source is 525nm)

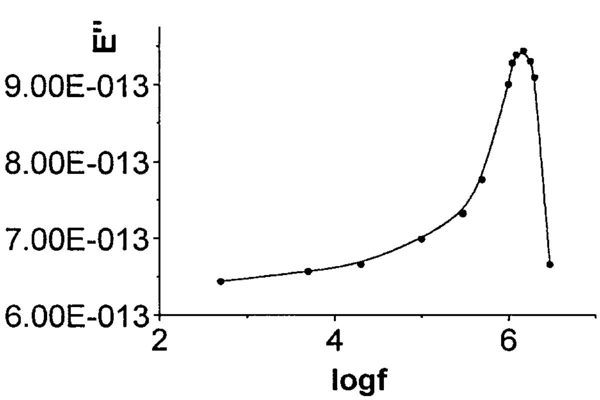

Fig3. A curve of dielectric loss values (ε '') versus logarithmic scale of experimental frequencies.