

The Topography and Structure Of Silver Bromide Grain Surface Modified By Metallic Sulfide Particles

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Abstract

A cubic AgBr emulsion is sensitized by $\text{Na}_2\text{S}_2\text{O}_3$ and by nanosized PbS separately, and is subsequently developed with a diluted developer to observe the grains' topography by SEM after development. The results disclosed that the initial developing site of PbS sensitized emulsion is quite different from that of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized one, and their dynamic process of development is also different from each other. Developing method also affects the topography of AgBr grains with a same developer. A disappearing process by electron injection under SEM is observed.

Introduction

We have previously reported that silver halide emulsion could be chemically sensitized by nanosized metallic sulfide¹⁻⁴. It was found that the sensitivity of metallic sulfide sensitized emulsion is higher than that of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized emulsion. We presumed that the number of sensitization speck is less and the speck's distribution is more concentrated on a AgX grain of metallic sulfide sensitized emulsion than on that of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized emulsion. In order to reveal the process of latent image formation, this report will give some information about the topography and structure of silver bromide grain surface modified by metallic sulfide particles after development.

Experiments

A cubic silver bromide emulsion was used in this experiment, and the edge length of AgBr grain is about 0.8 μm . A gelatin solution of lead sulfide particles was employed as chemical sensitizer of the AgBr emulsion, and the particle size is less than 10 nm. The preparation method refers to reference 3.

One group of the treated emulsions was directly coated on a stainless steel stage, then removed gelatin with an enzyme, exposed with a flashlight and developed with a diluted developer. This method is classified as on-stage development here. The developer formula is listed below.

Another group of treated emulsions was first coated on an ester base, exposed with a flashlight, developed with the same diluted developer as above, removed gelatin with an enzyme, and then transferred onto a stainless steel stage. This method is classified as out-stage development here.

The on-stage and out-stage specimens were subsequently observed under a HITACHI S-4300 Scanning Electron Microscope (SEM).

The diluted developer formula is: 0.25 gram of metol, 1 gram of ascorbic acid, 0.1 gram of potassium bromide, 3.5gram of sodium metaborate, and water to 1000 ml.

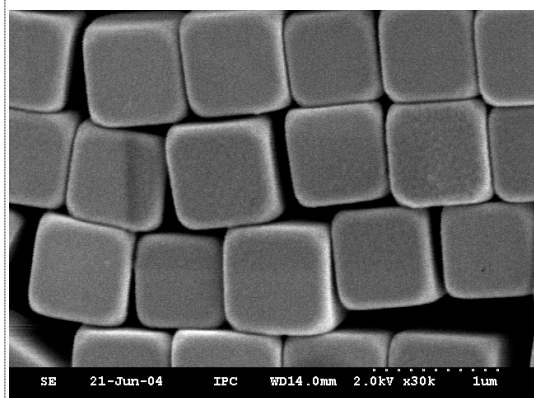
Results

Figure 1 demonstrates the topography of the on-stage developed AgBr grains. The corresponding emulsions were sensitized with equal molar fraction of $\text{Na}_2\text{S}_2\text{O}_3$ and PbS within equal ripening period, and the three emulsions were developed at the same diluted developer within equal time.

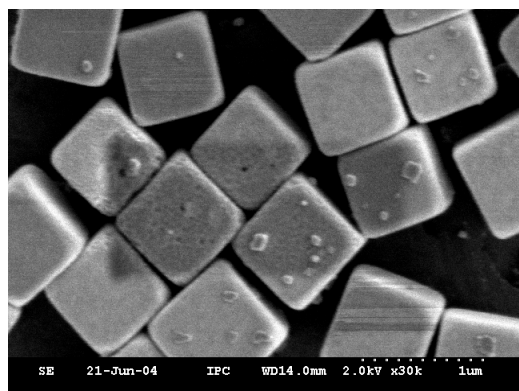
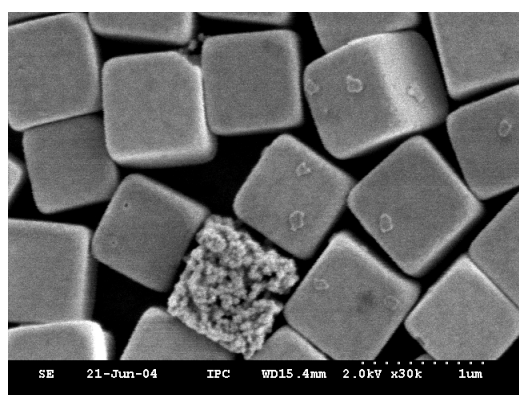
Figure 1a shows that the unsensitized AgBr grains kept undeveloped.

Figure 1b reveals that some AgBr grains sensitized by $\text{Na}_2\text{S}_2\text{O}_3$ were partially developed, and the size of developed specks on grain surface is different with each other. This phenomenon hints that there are many developing center on the grain surface and their developability are diversified.

Figure 1 On-stage developed AgBr emulsions



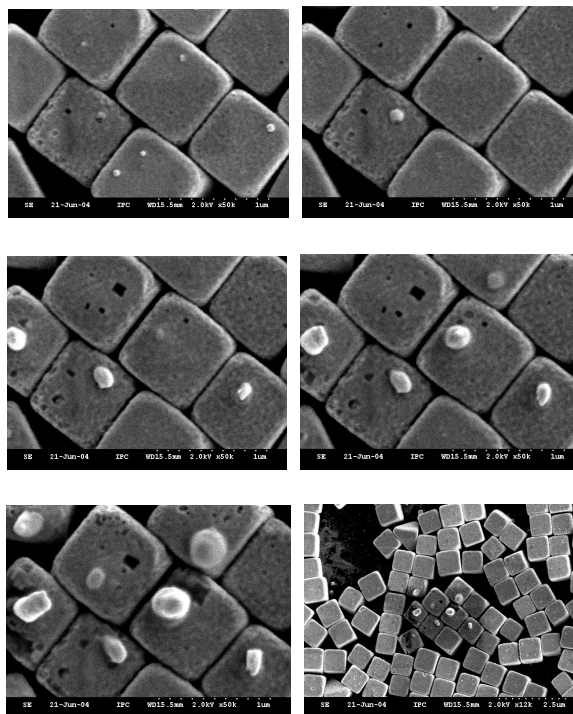
a) Unsensitized AgBr grain

b) $\text{Na}_2\text{S}_2\text{O}_3$ sensitized AgBr grain

c) PbS sensitized AgBr grain

Figure 1c demonstrated that some AgBr grains were partially developed, some were completely developed, and some kept undeveloped. The developed specks' sizes on a partially developed grain were about the same with each other, and a less number of developed specks on a PbS sensitized grain were observed than that on a $\text{Na}_2\text{S}_2\text{O}_3$ sensitized one. This may imply a uniform size

Figure 2 Silver disappearing and regenerating process under electron beam of SEM



distribution of sensitizing specks. The completely developed grain may hint that it has higher sensitivity than others or its developing speed is much faster than others, especially comparing with that of the unsensitized and the $\text{Na}_2\text{S}_2\text{O}_3$ sensitized AgBr grains. The completely developed grain also demonstrated that the developed silver is much compact and there is not any out-stretched silver filament. This may be resulted by the on-stage development on electron conducting stage such as stainless steel stage. Compact developed silver was not observed in an out-stage development specimen on ester base.

Figure 2 demonstrates the on-stage developed silver specks' disappearing and regenerating process under electron beam of SEM. The silver speck's disappearing process was also found on out-stage developed specimen except that its silver-disappearing speed is much slower than that of the on-stage specimen. The silver specks' disappearing process means that the developed silver speck is oxidized by electron injection.

Figure 3 discloses the dynamic developing process of unsensitized cubic AgBr grains. It demonstrates that the development speed is a relatively slow comparing to the sensitized emulsion mentioned below and the developed silver embryos are mainly located on the surface and corner. This implied that latent image is preferentially formed on the surface and corner of the

Figure 3 Dynamic development (out-stage) of unsensitized emulsions.

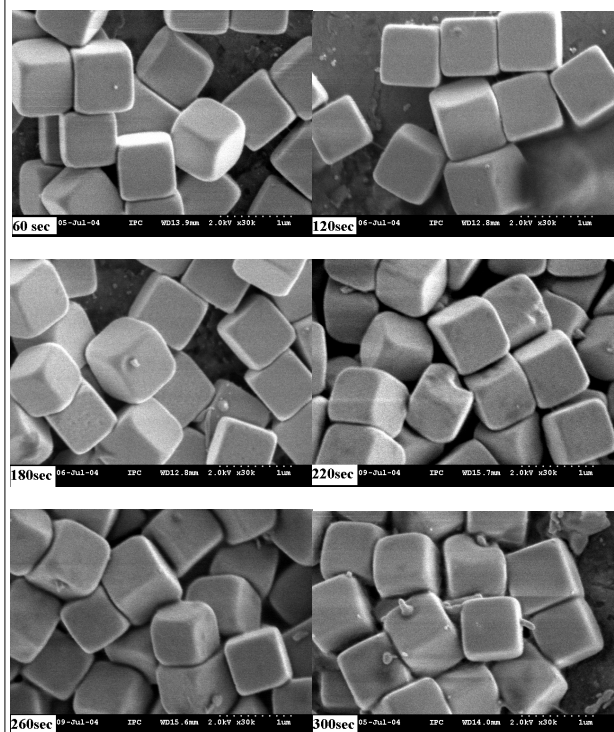


Figure 5 Dynamic development (out-stage) of PbS sensitized emulsions.

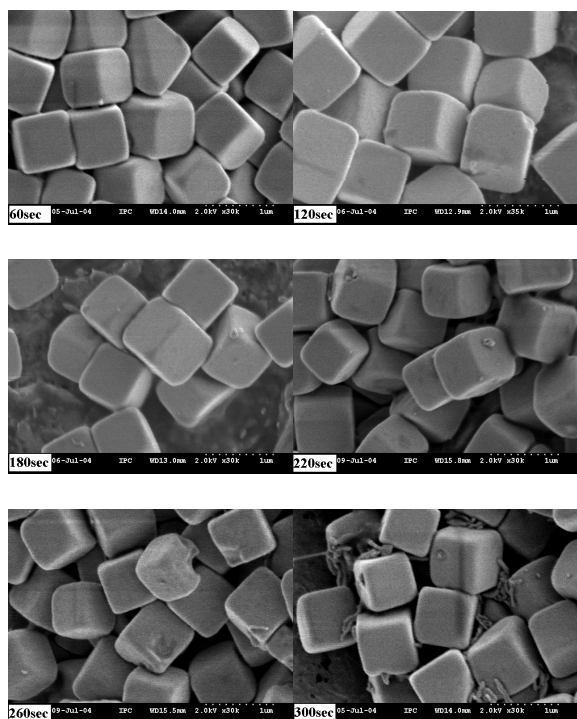
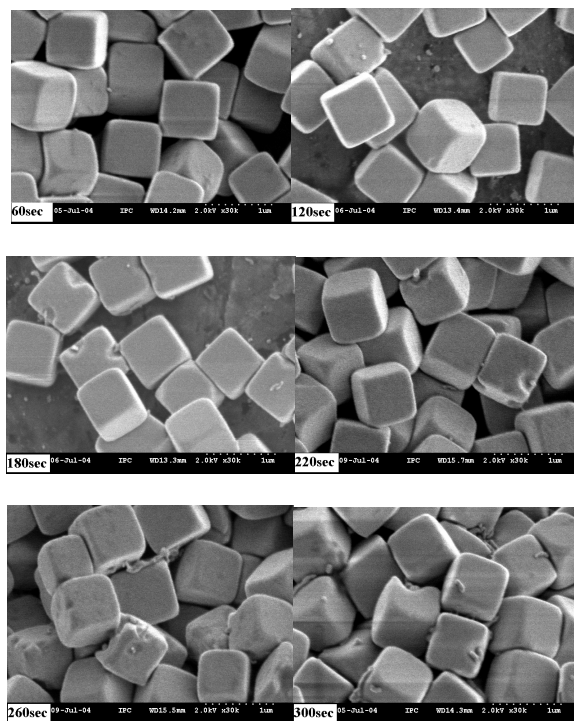


Figure 4 Dynamic development (out-stage) of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized emulsions.



unsensitized emulsion. It is also observed that the silver shape of out-stage developed specimen is different from that of on-stage developed one.

Figure 4 reveals the dynamic developing process of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized AgBr grains. The experiment steps are same as that of figure 3. It shows that the developed sites are concentrated on the edge of grains, and a very small amount of developed sites are on the surface. This phenomenon implies that the latent images prefer to form around the edge of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized cubic AgBr grains.

Figure 5 demonstrates the dynamic developing process of PbS sensitized AgBr grains. The experiment steps are same as that of figure 3 either. The micrograph shows that the initial developing site is mainly situated at the corner and a less amount of them at the surface. This suggests that the latent image site is quite different from that of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized AgBr grain but similar to that of unsensitized one. Furthermore, the development speed of PbS sensitized emulsion seems a little slower than that of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized at the starting stage, but much faster at the late stage by comparing the size of nicks or embryos by developing process. After 300 seconds of development, you can observe just some silver embryos at unsensitized and $\text{Na}_2\text{S}_2\text{O}_3$ sensitized AgBr grains, but many long silver filaments interspersed among AgBr grains at PbS sensitized grains.

Conclusion

a) It is observed by on-stage development that there are a less number of partially developed silver specks on PbS sensitized grain than on $\text{Na}_2\text{S}_2\text{O}_3$ sensitized, and the specks' size of the former are more close to each other than that of the later.

b) A compact shape of silver clusters without any out-stretched silver filament. will be formed by on-stage development.

c) There is a disappearing process for the developed silver speck on grain surface to be exposed to electrons under SEM.

d) The development prefers to start from the surface and corner of unsensitized cubic AgBr grain, from the edge of $\text{Na}_2\text{S}_2\text{O}_3$ sensitized one, and from the corner and surface of PbS sensitized one.

e) It seems that the initial development speed of unsensitized and $\text{Na}_2\text{S}_2\text{O}_3$ sensitized grains elevates smoothly, and that of PbS sensitized grains elevates slowly at the starting period and much fast at the later stage.

Acknowledgement

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Biography

Chun-hua Xu, Ph.D. student of Graduate School of Chinese Academy of Sciences.

Jin-pei Li got his B.S. degree in Chemistry from Sichuan University of China in 1987, now he is an associate professor of Technical Institute of Physics and Chemistry, Chinese Academy of Sciences. His major research field was silver halide photographic chemistry, now his research interest turns to photothermographic chemistry.