

Mechanism of Development in Nanometer-sized Silver Halide Emulsion

Suwen Liu, Jun Yue, Tanghong Cai and Maosen Chang
Department of Chemical Physics
University of Science & Technology of China, Hefei, Anhui, China

Introduction

Several mechanisms have been proposed for the formation of filamentary silver in the development of silver halide grains, but none is satisfactory[1]. Since filamentary silver is commonly obtained by developing silver halide emulsion in various developers for different time, the growth mechanism for developed silver filament remains one of the most perplexed questions that can't be evaded. The purpose of this article is to present some new observations and to provide some possible interpretations from a microscopic point of view.

Experimental

For our purpose, we take nanometer-sized AgBr/I emulsion in which the average diameter of the silver halide grain is about 20nm in our study[2]. The examination by TEM after development carried out under different developing conditions can be summarized as follows:

a)Nearly under each developing condition, filamentary silver is formed commonly with 20nm in diameter and several times that in length, which depends on the sort of the developer and the time of the development. It's easier to obtain filament from high-contrast developer than from fine-grain developer, and longer time of development leads to the thicker filament. From the difference of the contrast on the TEM photographs, we can tell the nonuniform density of the filament.

b)Accompanying with the formation of the nanometer-sized silver filaments, the nanometer-sized silver particles, diameter in range from 20nm to 30nm, are obtained in the developing process. Short-time development yields quite a few low-contrast particles which change into much denser ones after longer development time. Some particles resemble a bead with an aperture passing through the center of it. After long-time-development (at least eight minutes), the particles appreciably grow larger and their surfaces become rough and unregular.

c) On TEM photographs, we found some spherical silver particles with low contrast and uniform density after the emulsion is developed for about 30 seconds. Some silver filaments (especially the short ones) which look like multi-kerneled peanuts seem to be the combination of several fine silver particles.

Discussion

In the experiment we studied, nanometer-sized filament of silver is formed from nanometer-sized silver halide rather than from large silver halide grain. Thus, it's obvious that the diffusion-extruding mechanism proposed by Berry[3] can't convincingly explain how the filament grows from the nanometer-sized AgBr/I emulsion, neither can the mechanics proposed by Metz[4] or other authors.

At the beginning of the development silver atoms are produced at a certain point. This step is similar to the model proposed by Berry[2]. Both Berry and Skillman[5] suggest that it is the limited diffusion of silver that first causes the growing sphere to begin to elongate. As the developer transfers electrons to a silver halide grain during the reduction process, the grain is negatively charged, and then the particle consists of two parts, the semi-conductor of AgX crystal and the conductor of initial silveratoms. According to the principle of the charge distribution, the electrons will concentrate at the conductor part. The steeper curvature there also contribute to this result. Thus, it's at this point that the silver part most likely continue to grow from the reduction of the silver ions, whether derived from silver halide grains or from the solution. In addition, the incipient silver atoms having insufficient time to incorporate into lattice , may be noncrystal with higher surface activity. The curvature at the initial silver is great also, resulting in the high surface activity. All these general considerations contribute to speed up the rate of the formation of the silver atoms at points on the newborn surface and thus the filaments grow.

However, after the prolonged time of development, there're more dissolved silver ions that have little selectivity for the surface of the filament, thereby increase the proportion of uniform deposition of silver on the surface of the filament increases and the silver filaments are thickened or maybe repressed. In fact, there are some nanometer-sized silver particles formed at the same time of the formation of the nanometer-sized silver filament.

We suggest that at the first step of the development, some silver halide grains are encircled by the developed silver atoms reduced from the silver ions in the grain itself. In the process of the further developing, the silver ions of the silver halide inside are reduced and hence the halogen ions flow into the solution through the silver periphery. This can just explain the enlargement of the particle after long-time-development and the appearance of the particle with a hole. Experimentally, we also find hollow particles shaped like balloons. However, what still puzzles us is how the halide ions inside these “balloons” flow out during the further developing process.

Only one filament is produced from one nanometer-sized silver halide grain, Skillman[5] has shown that silver ions from several grains may contribute to the formation of a single nanometer-sized silver filament. In our experiments, the TEM graphs show that some short filaments look like the combination of several particles. We assume that they are actually the aggregation and link of several developed nanometer-sized silver particles or filaments that have insufficient time to grow. According to the DLVO theory[6], the aggregation among the initial silver particles is dependent both on repulsion of the electrical double layer and on Van der Waals attraction. The resultant curve of Van der Waals attraction and interparticle repulsion shows one maximum and two minima. When the two particles approach, overcome the potential barrier between the two minimum points and reach the first point where the potential energy is lowest, they stick together.

References

1. Liu, Yuansheng et al., *J. Photogr. Sci. Photochem. China*, **3**, 46,(1983).
2. C. R. Berry, *Photogr. Sci. Eng.*, **13,** 65 (1969).
3. Liu, Suwen et al., *J. Photogr. Sci. Photochem. China*, **14** (3), 256 (1996).
4. H. J. Metx, *J. Photogr. Sci.*, **20,** 111 (1972).
5. D. C. Skillman, *Photogr. Sci. Eng.*, **19**, 28 (1975).
6. P. C. Hiemenz, *The Principle of Colloid and Surface Chemistry*, Marcel Dekker ONC., 1977, 613-616.