Permanence of Size Distribution of Silver Nanoclusters Produced in Silver Halide by Light or Chemical Fogging and Partly Oxidized with Photolytic Halogen

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Abstract

The regular multistepped structure of characteristic curve (CC) has been recently shown to correlate to the atom-by-atom growth of the largest latent image (LI) centers in every silver halide microcrystal with light exposure. It was derived from a simple stochastic process of LI formation when the smallest particles only were capable to move and join one another or a larger immobile particle, or to break away from them. A silver LI formed by chemically produced fog nanoclusters after their partial oxidation by photolytic bromine has been shown to display the same steps in developing activity as photolytic silver in the "bromide" LI state. After treated with a thiocyanate solution prior to development, the exposed layer has doubled the frequency of the steps, indicating the LI transition to the "non-bromide" state. The same nanocluster size distribution was concluded to keep for the common LI formed with excess photolytic halogen or without it as well as for the chemical fog centers transformed by photolytic halogen into a direct positive LI. The deciding generality of all the three processes is discussed to form or destruct silver nanoclusters through random addition or separation of only moving mon- or two-atomic species.

Introduction

The multistepped structure of the *D-logE* curves of photographic materials[1-3] has been recently shown to possess a regular character[2,4] that had a suggestive correlation with the simulated atom-by-atom growth statistics of the largest LIC in a grain[5]. The probabilistic coalescence process of mon- and two-atomic species that is capable to generate such statistics seem to be applicable in principle not only to the photolytically produced metal atoms but likely also to those produced by silver halide reduction under action of chemicals.

A way to prove the generality seems to test a direct positive emulsion with silver nanoclusters produced by a silver salt reduction in a stannite solution. After the emulsion is exposed by light, the fog centers are partially oxidized by photolytic halogen mon- or two-atomic species and transform into a LI. It could be therefore expected that the characteristic properties of the regular multistepped structure of CC are for direct positive the same as for negative emulsions considered earlier. The relative weights of the individual steps of development rate growth depend on many technological factors and are not characteristic in the sense. In contrast, the typical spacing value between the steps is rigid against the factors and should remain unchanged for the two LI kinds. Its change to another characteristic value should occur under similar conditions, for instance, due to the silver salt conversion capable to violate enough the known crystal lattice correspondences of silver bromide microcrystals to silver.

Experimental

A non-sensitized monodisperse *AgBr* (2.0% *AgJ*) emulsion layer with 0.10 mkm microcrystals and the size variation coefficient about 0.08 has been exposed and developed in a solution of 1g/l sodium sulfite, 8g/l methol and 40 drops of 10% NaOH for 40 min at the temperature 20 ± 0.3°. The same emulsion, previously undergone a stannite fogging, has been also exposed to light (about two orders of magnitude more than above) and developed for 15 min in a solution of 50 g/l sodium sulfite, 0.6 g/l hydroquinone, and 50 g/l sodium carbonate. Both the bromideless developers did not shift characteristic curves along the *logE* axis [5,6]. The hydroquinone developer acting in a contrast cannot be applied to the negative emulsion due to an unacceptable development fog.

The pre-fogged emulsion has been also treated with the 0.75 g/l potassium thiocyanate solution for 30 min, 1 h, 2 h, 4 h and 24 h and washed for 30 min in distilled water before processed in the hydroquinone developer. Such a treatment usually results in conversion of silver halide into silver thiocyanate accompanied by a partial loss of salt due to its dissolution at a prolonged treatment[6].

The optical densities were measured with a densitometer of differential type. Its measuring wedge was calibrated with a mean-square error of about 0.005 density units. The relative exposures of sensitometer fields were known also with the same accuracy.[2,4] For the deciding shape peculiarities to be expressed more clearly, a CC underwent a numerical derivation with respect to *logE*, using five nearest values of optical density, *D*, and the "gradients," $g = dD/dlogE$, were calculated. Their mean-square error was about 0.05 gradient units.

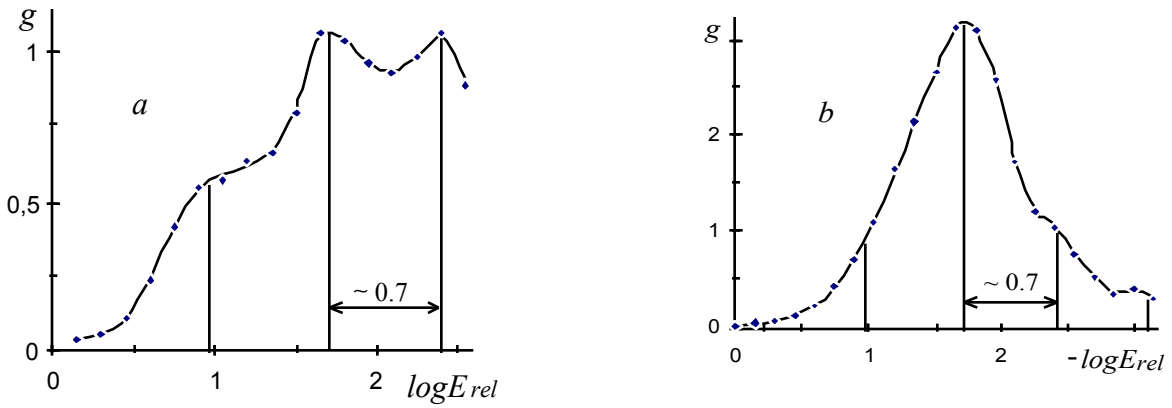

Figure 1. The derivative of characteristic curve of AgBr(2.0% AgJ) emulsion with respect to logE in dependence upon the $logE_{rel}$: a) negative version; b) direct positive version produced from the negative emulsion with the chemical pre-fogging

The curves of Figure 1, and curve 1 on Figure 2 are an average of four parallel tests. The curve 3 on Figure 2 is an average of four curves that correspond to 1, 2, 4 and 24 h treatment in the *KSCN* solution before the development.

Latent image produced by light-induced destruction of chemical fogging centers

Figure 1 displays the *g-logE* obtained for negative and direct positive versions of the emulsion considered. Both the curves correspond to the same multistepped structure of characteristic curves that is typical to silver bromide emulsions.[4-6] Although the relative weights of individual steps differ in both the cases, the spacing between the adjacent steps remains close to 0.7 B.

The relative as well as absolute exposure scale on Figure 2 is the same for all the curves considered. The conversion of silver bromide microcrystals into silver thiocyanate originates some new regular curve shape peculiarities that indicate the same doubling of steps as observed earlier for similarly treated negative emulsions [6]. The new value of interstep spacing is about 0.35 B. It is typical to other non-*AgBr* photographic emulsions [4,5].

The data obtained indicates that the chemical fogging produces silver nanoclusters of the same size statistics and their partial oxidative destruction by photolytic halogen does not change it. It would be difficult to imagine the two consequent chemical processes to give the same structure of the characteristic curves as usually in another way. The direct positive LI possesses the same size-statistical, structural and epitaxial properties as common negative LI.

Although the common LIC formation is always followed by partial rehalogenation, it demonstrates the same regular multistepped structure of *D-logE* curves as the mathematical simulation of simple coagulation of moving mon-atomic and two-atomic species predicts[5]. Special computer simulations have resulted in the size statistics of negative LIC that has not varied under oxidative action of separated photolytic halogen. The efficient emulsion speed only significantly decreased.

Summary

The size statistics of silver nanoclusters formed by photolysis, or by chemical reduction of silver halide, or by the partial oxidation of the latter with photolytic halogen result in the multistepped structures of characteristic curves with the same spacing between the individual steps of the development rate growth with the light exposure. The only general feature of the processes seems deciding with respect to their similar influence on the LIC size distribution and thus on the development rate. Each of them occurs as a stochastic succession of random additions of moving mon-atomic and two-atomic species to immobile particles of larger size as well as their break-off acts of the immobile particles.

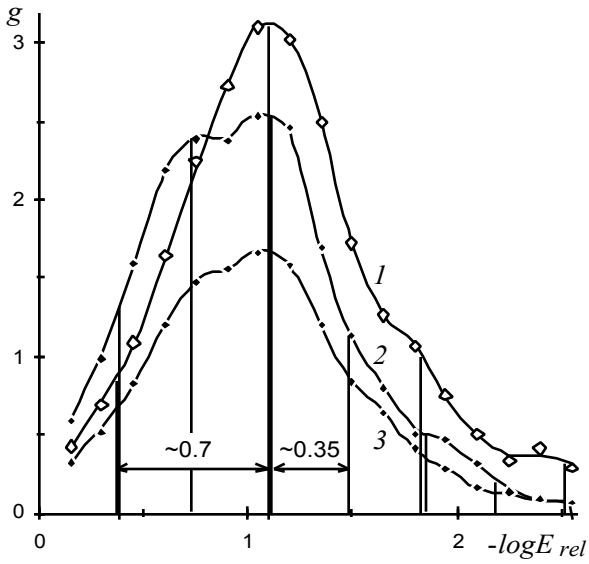

Figure 2. The gradient curves of the direct positive emulsion: control (1), and converted in 0.75 g/l KSCN solution for 30 min (2), and an average (3) of curves that correspond to 1 to 24 h conversion in the solution.

References

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