

Nonselective reduction of AgBr emulsion. Correlation between concentration of silver on the surface and microcrystals speed.

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Abstract

Physical and chemical base of photographic process on the main stages (chemical sensitization [CS], exposure and development) is connected with reactions of reduction of emulsion microcrystals (MC). These reactions proceed up to different levels and are often combined together. The evolution of silver during chemical sensitization determines the formation of sensitivity centers and fog centers and therefore this process is directly connected with photographic speed formation. The analysis of original results and literature data on the problem of association and redistribution of silver atoms during formation and growth of silver specks is given. The correlation of structure and centers compositions with sensitometric characteristics is discussed. It is noted that the data connected with mechanisms of individual stages are often contradictory. The alternative approaches to the nature and sizes of latent image centers which are able to initiate the total reduction of emulsion MC during development process are also discussed.

Introduction

The problem of the nature and size of silver clusters capable of initiating development of emulsion grains remains far from being solved. An alternative concept - that oligoatomic clusters of silver or colloidal particles - was proposed in the work of Reinders¹ in his studies of "physical" development. Electron microscopic observation gave a sheer evidence of colloidal particles². In the model experiments on physical development of deposited silver layers the critical size often corresponded to oligoatomic cluster size³. As to nucleus critical size in conventional ("chemical") development there have been different points of view.

We can find a solution of scientific and practical aspects of CS problem by a systematic theoretical and experimental investigation of the evolution of silver on the surface of emulsion silver halide MC, of the influence of impurities

on the aggregation process, etc. This can be a base for development of optimum methods for photographic speed formation and for search of new sensitizers.

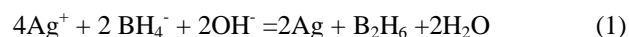
The most "pure" type of CS, when reduction of the emulsion MC surface is not accompanied by some side reactions, is reduction sensitization (RS). It seems that this is the reason for appearance in the last time of a number of works dedicated to investigation of RS. In the present work the morphology of silver created as a result of nonselective reduction of the model MC surface is studied. It seemed very important to obtain an information about topography of the reduction centres of the heterogeneous process in the initial step of which RS is observed.

Experimental

NaBH₄ was used as an active nonselective reducing agent. The plates with the emulsion layer of 30 mkm thickness were processed by the solutions. The influence of the concentration of the alkaline (1% KOH + 1% KBr) aqueous solution of NaBH₄ in the interval of 0 - 5*10⁻⁴ M/l and reduction time (1-16 min) at T=20°C on morphology of reduced silver on the MC surface of the primitive AgBr(I) (molar ratio of AgI 4%) and AgBr emulsions was studied. MC of the first emulsion synthesized by the single jet method were a mixture of tetrahedrons and complicated configurations a wide size distribution (with mean diameter 1.1 mkm and Cv=30.6%). The second emulsion obtained by the double jet method consisted of homogeneous cubic MC with a small twin forms impurity (with average size 0.55 mkm and Cv=9.9%). The habit and sizes of the reduced silver particles were controlled by transmission electron microscopy on one step carbon replicas⁴.

Discussion.

The emulsion MC reduction reaction can be described by an equation



The equation (1) describes a total reaction effect. A real mechanism of the topochemical process is much more complicated and seems to include several steps: 1) reagent chemisorption on the MC surface and near surface gelatin layer; 2) the transformation act itself; 3) formation and growth of silver molecular clusters up to some critical size; 4) their transformation into metallic phase; 5) growth of metallic colloidal silver particles.

In the process of MC surface reduction a formation of reaction local centres was discovered as small dispersion silver particles with average size 10-20 nm. Corresponding microphotographs of replicas with extraction are presented on fig.1.

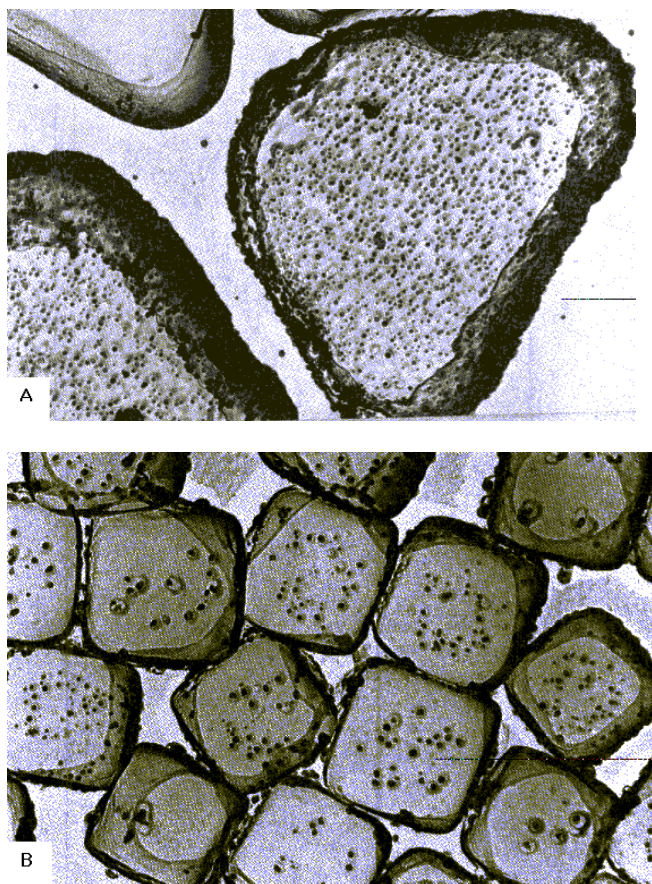


Figure 1. Microphotographs of MC replicas with the particles of reduced silver obtained as a result emulsion processing by 10^{-4} M solution of NaBH_4 , $T=+20^\circ\text{C}$: a - MC AgBr(I) (molar ratio AgI 4 %) $100 \cdot 10^3 \times$; b - MC AgBr $100 \cdot 10^3 \times$.

The observed particles of reduced silver had a form close to spherical. With increase of reaction time and reagent concentration their average size had some increase reaching a saturation. It is characteristic that the measured values changed in relatively narrow interval and practically did not depend on size and form of used MC (fig.2). Metallic silver formed during first minutes of reaction was unevenly distributed on the MC surface, as the separate

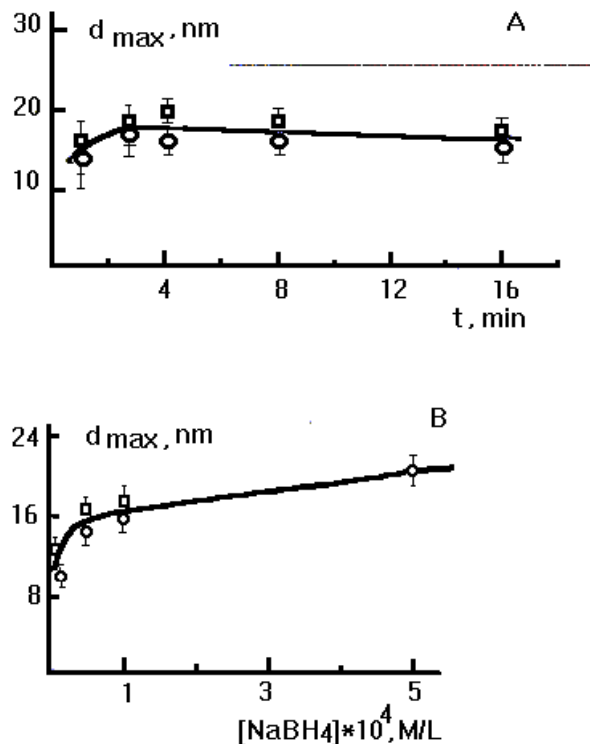


Figure 2. Dependence of the average particle size of reduced silver on the time of reaction with 10^{-4} NaBH_4 solution (a) and on the concentration of reducing agent (b). $T=+20^\circ\text{C}$. \sim - MC AgBr(I), \circ - MC AgBr(I) (molar ratio AgI 4 %).

particles or compact groups of 20 - 40 particles. The possible reasons for that are the uneven reagent distribution in the studied system, side processes, e.g. gelatin reduction, and separation of some silver particles from their initial positions at replica separation and washing in processing. Significant unevenness in reduced silver particles distribution existed after 4 min. reaction time at NaBH_4 concentration up to 10^{-4} M/l. Obtained microphotographs showed both MC with high particle concentration and grains practically not containing silver. The areas with high concentration of reduced silver (with the size ~ 600 nm) in the case of tetrahedral and plane MC were often situated on the edges and side surfaces of the crystals. On the contrary, in the case of cubic MC any preferable localization of metal particles on the edges was not observed.

With the increase of the the reaction time the unevenness in the particle distribution on MC decreased. Simultaneously on the later steps of the process particle coagulation intensity increased.

Fig. 3a presents a histogram of particle size distribution on six randomly chosen cubic faces that model the total surface of silver bromide MC after processing in NaBH_4 solution with a concentration 10^{-4} M/l. This distribution

corresponds to average particle size $d_{max} = (17 \pm 1)$ nm and partial density $2.6 \cdot 10^{-4}$ nm⁻². In average such particles contain $1.8 \cdot 10^5$ atoms. The resulting distribution of the number of atoms is strongly shifted to the small number of atoms side. About 40.4% of all particles in the interval $0-10^6$ atoms contained up to 10^5 silver atoms. Three-dimensional 3D histogram illustrates a character of silver particle size evolution in the first 1 min. of reaction.

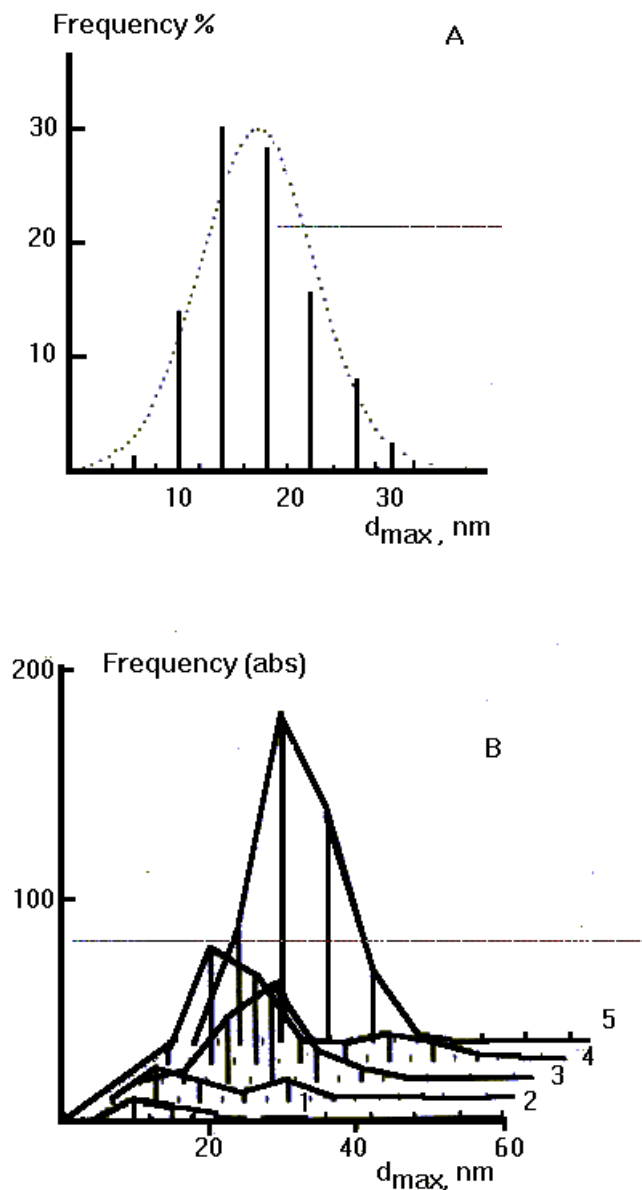


Figure 3. Histograms of particle size distribution of reduced silver on the surface of AgBr MC processed by 10^{-4} M NaBH₄ solution, $T=+20^{\circ}$ C: a) time of processing by the reducing agent is 16 min., b) three-dimensional histogram, characterizing evolution distribution function of silver particle size in the process of reduction reaction; numbers correspond to different times of reaction: 1 (1), 2 (2), 4 (3), 8 (4) and 16 min (5).

It follows from the obtained results that having autocatalytic character plural nucleation in the process of nonselective MC reduction leads to the formation of the surface net of reduction centres actively competing in small local surface areas. Due to high speed of chemical transformation and nuclei growth their sizes soon start to exceed a value corresponding to the transition from the molecular clusters to the colloidal particles. The forming aggregates of reduced silver lose their mobility and get stabilized, a contribution to the growth processes of the particles due to coalescence decreasing.

In our experiments the sensibility centres (silver clusters with small number of atoms) were formed during short periods of time on the initial step of the reaction and was observed only in the case of diluted solutions of the reducing agent (10^{-5} M/l). In this case the 10-15 times growth of speed was registered during 10-15 minutes for both emulsions.

From our point of view, the presented results wonderfully complement the data of the last works by R.Hailstone dedicated to sensitometric and spectral studies of RS for model emulsions.

The characteristic spectral changes noted in these works (appearance and growth of absorption intensity of molecular silver in the process of CS with the maximum at $\lambda = 475-480$ nm; clearly shown relation between speed and the value of absorption on the initial steps of CS for all regimes) are undeniable proofs of existing of high concentrations of molecular clusters on the surface of sensitized real emulsion MC.

We have all the reasons to suppose that in both cases of RS the surface concentrations of silver clusters and their size distributions are very close. In our experiments the maximum of photographic speed of the layer came at $t = 5-18$ min., meanwhile after 15-20 min. of reduction the surface concentrations of silver, determined by the analysis of electronmicroscopic shots, was 100 atoms/nm² ($\sim 10^{16}$ atoms/sm²). Even if we suppose that surface concentration of silver atoms has an exponential growth in the process of reduction, we obtain that surface concentration of Ag corresponding to the photographic speed maximum can be 10-20 atoms/nm² ($\sim 10^{15}$ atoms/sm²) that is very close to the data by Mitchell⁵.

It is difficult to image that at such high concentration and autocatalytic character of silver reduction it can be evenly distributed as Ag₂ - Ag₃.

Suggested treatment of our experiments has one convincing argument. It is a discovered change of absorption spectra of reduced emulsions after their exposure. In the case of short exposures⁶ a noticeable decrease of short-wave absorption (475 nm) and appearance of absorption at 550 nm were observed. Such phenomenon can be considered as a direct proof of photostimulated transformation of oligoatomic silver clusters –“primary centres” of K.V.Chibisov-E.A.Galashin into “secondary”,

capable to induce development. If we consider the results of papers^{7,8} as justified, then the absorption peak at $\lambda=475$ nm correspond silver cluster into AgBr matrix with $d \ll 1,6$ nm and consisting of $\ll 130$ Ag atoms, to the peak at $\lambda = 550$ nm correspond silver clusters into AgBr matrix with $d = 3,8$ nm and consisting of 1700 Ag atoms or silver clusters in gelatine $d=10,3$ nm and consisting of $3,3 \cdot 10^4$ atoms.

Acknowledgment

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References

1. W.Reinders, J.Phys.Chem., **38**, 783(1934).
2. E.P.Senchenkov, E.A.Galashin, Y.V.Fedorov and K.V.Chibisov, J.Inf.Rec.Mater. **10**, 3 (1982).
3. P.Fayet, F.Granzer, G.Hegenbart, B.Pischei and L.Woste, Z.Phys. D.Atoms, Molecules and Clusters, **3**, 299(1986).
4. A.E.Galashin, N.K.Zaitcev and V.P.Oleshko, Zh nauchn. fotogr. kinematogr., **34**, 332 (1990) (Rus.).
5. J.M.Hedgec and J.W.Mitchell, Phil.Mag., **44**, 1357 (1953).
6. S.Guo and R.K.Hailstone, Proceedings of IS&T's 48th Annual Conference, Washington D.C., May 7-11, 1995, p.197.
7. S.F.Chernov and V.N.Zakharov, J.Mod.Optics, **36**,1541(1989).
8. S.F.Chernov and V.N.Zakharov, J.Phot.Sci., **44**, 50 (1996).