Percolation as Possible Mechanism for Ulra-Fast Silver Reduction Under Intensive External Influence

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Abstract

Up to this moment there exists a lot of experimental data which indicate the possibility of high speed electron injection into the grain based on both inorganic and organic salts of silver (e.g. electrolytic reduction of emulsion grains [1], flash photolysis of silver bromide and silver stearate nanosols [2, 3], ultra fast reduction of AgBr nanocrystals [4, 5]). These phenomena can not be described by the use of traditional schemes of silver nucleation containing ionic steps of the process, since the experimentally observed speeds of electron injection into the grain are six orders of magnitude higher than the ones necessary for ionic processes. Such high speeds can be only explained by the processes in the electronic subsystem. In paper [6] it was proposed that the silver nucleation process in silver bromide was the result of electron supersaturation in the conduction band. Taking into account the structural correspondence principle by Dankov [7] we propose the percolation mechanism for ultra-fast silver reduction (aggregation) under powerful light beams. This mechanism can be possible explanation for appearance of high optical densities for visible part of spectrum in $10^{-8} - 10^{-3}$ s time interval.

Introduction

Up to this moment there exists a lot of experimental data which indicate the possibility of high speed electron injection into the grain based on both inorganic and organic salts of silver. These phenomena can not be described by the use of traditional schemes of silver nucleation containing ionic steps of the process, since the experimentally observed speeds of electron injection into the grain are six orders of magnitude higher than the ones necessary for ionic processes. Let us consider corresponding examples.

In paper [1] we considered a mechanism of electrolytic reduction of emulsion grains and the Rothstein effect. One of the general features of this mechanism consisted in fast speed of reduction which disagreed with the rate of ionic process. If, for instance, electroreduction of emulsion grains proceeded according to the Guerney-Mott or Mitchell mechanism, then the limiting stage of the silver cluster formation would be the ionic one with a duration of $10^{-3} - 10^{-5}$ s, and not less than 10^{-6} s, as follows from reciprocity failure. In this case the electron injection rate cannot exceed $10^{5} - 10^{6}$ s^{-1}, against experimental values of $10^{11} - 10^{12}$ s^{-1}. During the period of time in which, as commonly considered, an oligoatomic speck of latent image is formed the whole grain is developed.

The results of laser flash photolysis of a silver bromide nanoparticle dispersion, synthesized without and with silver stearate interface, were reported in [2,3]. Transient absorption spectra at various delay times following laser flash photolysis (30-ps pulse, 355 nm) were obtained. In both cases the transient absorptions the authors assigned to formation of Ag^{0} clusters. Absorbance change equal to 0.8 was obtained in 5 ns.

Experimental data for chemical reduction of ultra-fine grained AgBr crystals under the action of flash were presented in [4, 5]. High optical densities (D $\geq$ 1) were obtained in few milliseconds. Let us note that morphological investigation of developed silver suspensions established an absence of silver whiskers and presence of compact silver specks.

In this paper we will consider a model to describe ultra-fast reduction of AgBr nanocrystals, placed into redox solution, under the action of intensive actinic flash. A preliminary results were published in [8].

Percolation model of silver cluster formation under the action of intensive flash

One of approaches to describe a formation of silver specks in the theory of photographic process is a thermodynamic consideration by Moisar, Granzer et al. [6] According to this theory action of light leads to the electronic density supersaturation in the conduction band of AgBr. When this supersaturation exceeds a critical value, silver phase starts to appear as Ag$_n$ silver specks. Energy of formation of this silver nucleus can be calculated according to

$$\Delta G = 4\pi r^2\, \sigma - (4/3)\pi r^3 RTV_m^{-1} ln\{[e^-]/[e^-]_\infty\}, \qquad (1)$$

where σ is the specific interfacial energy of Ag/AgBr, V_m is the molecular volume of silver and r is the radius of the silver nucleus, $[e^-]$ is the stationary concentration producing supersaturation and $[e^-]_\infty$ is the electron concentration in AgBr conduction band before action of light. According to this theory all the events leading to silver phase formation takes place in the electronic subsystem of AgBr.

Let us note here the interesting result by Dankov [7] obtained in 1939 and called as structure correspondence principle of AgBr cation sublattice to the lattice of metallic silver. He noticed that AgBr space lattice can be transformed to the lattice of metallic silver without change of silver atom positions, {100} cube planes in $[Ag^+ - Br^-]$ lattice corresponding to {110} octahedron planes and {001} cube planes in [Ag] lattice. In accordance with this principle the distances between silver atoms in {001} cube planes do not change after bromine atom withdrawal from the lattice AgBr lattice and silver ion (e.g, from the interstial) taking its place. This atom "leaves the electron to the possession not only of one of his neighbors, but to the possession of complex of them" [7].

On the other hand Mitchell using statistic thermodynamic analysis [10] obtained that all usual electron traps were two shallow to trap photoelectrons that made conventional step by step process questionable. From the Mitchell's point of view the trap became effective only then "a molecule" Ag_2^+ has been formed (compare with the Dankov's complex!).

We propose that after excitation of electron by photon it is possessed by 4 silver neighboring ions in the regular positions of the lattice plane and by 5th ion taking position of bromine. Absorption of each photon leads to creation of such complex. The positions of such complexes on the surface are random, the higher the concentration of photons the higher is the concentration of these complexes. The neighboring complexes (we consider the complexes as neighbors if they have the common edge) create bigger complexes filling the surface of microcrystal. This picture corresponds to the usual percolation scheme, used in the theory of disordered systems [10]. For some critical concentration of photons (and correspondingly electrons and complexes) the percolation threshold is exceeded and we have a metallic grid covering the whole surface of the microcrystal. The concrete form of this percolation greed will be random and depends on the position of bromine ions that absorb the photons (and therefore on the positions of the created complexes).

We carried out computer modeling of reduction process described by the proposed percolation model and considered the formation of silver clusters for the case when the value of actinic photons varies from 1 to 1000000. For the fixed numbers of photons we determined the following functions: the total number of appearing clusters, the distribution function as a function of cluster size, the cluster distribution for the different atomic layers of the microcrystal, the size of the percolation cluster, the specific number of photons necessary to form the clusters of fixed size.

Conclusion

The mechanism of silver cluster appearance in the systems of this kind is based on the principle of structural correspondence of AgBr cation sub-lattice to the lattice of metallic silver. According to this correspondence the motion of silver ions is not necessary for silver cluster formation in AgBr microcrystals. The percolation mechanism is in agreement with the high speed of electron absorption by AgBr nanocrystals under external influence.

The obtained results give the possibility to analyze the processes taking place in such system and can be useful for development of different sensors, optical filters, thin layer indicators, photonic devices, the materials with variable light transmission in the ultraviolet and visible spectrum intervals.

References

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Biography

Dr. Valery Zakharov is a senior research fellow of the Laboratory of Structural Chemistry, Department of Chemistry, Moscow State University. He is an author and co-author of 85 scientific papers and patents. The fields of scientific interests are theory of photoprocess, metallic clusters, ODMR spectroscopy, integrated chemical systems.