Evolution of Silver Sulfide Centers on AgBr Microcrystals Surface during Chemical Sensitization

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Abstract

The structure of light sensitivity centers is investigated by Small angle X-ray scattering techniques (SAXS). The functions of particle size distribution $D_m(d)$ are computed from SAXS intensity curves. The model of a Ag_2S particles structure both in initial colloid and after introduction in the AgBr emulsion is suggested. Some peculiarities of clusters' structure change in sensitization process are revealed.

Introduction

It is considered, that the increase of photographic emulsions sensitivity at the sulfur sensitization is caused by formation on the emulsion microcrystals surface the Ag_2S clusters[1]. In the present work the sensitization was carried out by direct introduction of silver sulfide dispersion in the AgBr emulsion. By the purpose of work is to investigate the structure of Ag_2S clusters in the initial colloid and during sensitization process.

Experimental Techniques

The silver sulfide dispersion was received by a double-jet method on reaction of an ionic exchange between silver nitrate and sodium thiosulfate in absence of protective colloid. Received dispersion add to unsensitized AgBr emulsion and maintain in 4 hours at temperature 50°C. Layers are fixed in current of 20 minutes, dried up under vacuum and are investigated.

SAXS investigations were carried out using a KRM-1 camera with a slit collimation. Cu K - radiation (λ=1.5418 A) was used. The experimental SAXS curves were de-smeared[1] in order to eliminate collimation distortions. The functions of size distribution on the assumption of a sphe-rical form of the particles were computed from desmeared SAXS curves by the use of the principle of least squares coupled with Tichonov's regularization[2]. The FORTRAN-77 program package created by the authors was used[3].

Results and Discussion

It should be noted, that the computing of particle size distribution functions from SAXS data first of all requires to set the model of a scattering particles structure. At the first stage we have chosen (as a most simple and logical) the model of homogeneous spheres. The mass function of particle size distribution $D_m(d)$ obtained within the framework of this model for initial Ag_2S colloid is characterized by presence of two maxima (figure 1a). Since the presence in the given system of two various ensembles of homogeneous spheres is represented improbable we have assumed, that the additional maximum on a size distribution curve is connected with the inhomogeneity of scattering particles (themselves).

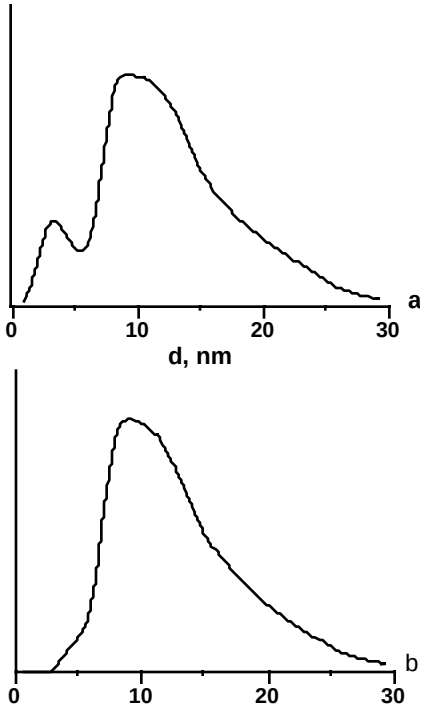

Figure 1. Mass functions of particles distribution on the sizes in initial colloid: a - account on similar spheres, b - account on model of a type "nucleus - environment" (the ratio of densities of a nucleus and environment is 0.78, the ratio of radiuses of a nucleus and environment is 0.70)

According to this a little bit complicated model of the scattering cluster structure was offered, namely: a two-phase "core-shell" spherical particle with radial-symmetric distri-bution of scattering density. Varying of this model para-meters (ratio of radii and densities of an internal nucleus and environment) allows us to describe initial colloidal system of particles by the monomodal function $D_m(d)$ (figure 1b). It is remarkable, that the optimum ratio of a core and shell density (about 7:10) qualitatively corresponds to a ratio of Ag_2S and silver density.

The average value of an particles external diameter, ob-tained from $D_m(d)$ curve is 16 nm. At the same time, the size of Ag_2S crystallites appreciated from X-ray diffraction data by Scherrer's method, is 13 nm, that qualitatively corre-sponds to the average size of particle cores. Thus, it is possible to assume, that the structure initial clusters is char-acterized by presence of a superficial layer of a little bit grea-ter density by thickness about 2-3 nm. From the phase com-position point of view, this layer may be a phase of silver, or a phase of nonstoichiometric enriched by silver sulfide.

Our experiment has shown that the dispersed structure of clusters in the sensitization process undergoes significant changes: the characteristic size of scattering inhomogeneities appreciably decreases, the curve $D_m(d)$, computed on homo-geneous spheres, becomes narrower and has more oscil-lations. By using of two-phase model mentioned above the $D_m(d)$ function also remains multimodal at any values of varied parameters.

We have assumed, that the complex character of $D_m(d)$ function is connected with morphological peculiarities of scattering particles. Thus, we considered the $D_m(d)$ computed on homogeneous spheres as a kind of characteristic function, describing a particle of the certain morphology. (It is known, that $D_m(d)$ computed on homogeneous spheres is proportional to the third derivative of Debye's characteristic function[4].)

Computer simulation in a class of three-parametrical homogeneous bodies, have shown, that the $D_m(d)$ functions rather similar with experimental can be obtained for monodispersed system of particles of the certain form. The SAXS intensity curves of simulated particles were computed using Debye's formula[5], then these curves were processed[3] to obtain required $D_m(d)$ functions. First of all it is necessary to note, that the isometric bodies (spheres, cubes, ellipsoids, rectangular prisms, bipyramids etc.) for the most part have appeared obviously improper for the description of experimental data. Much the best similarity to experiment was observed for such bodies as half-spheres, flattened half-ellipsoids pyramids or cones of height which is about twice less than diameter of their basis (it is remarkable, that all of these bodies are characterized by absence of a horizontal plane of symmetry). Varying dimensional and morpho-logical parameters we have constructed a number of similar among themselves models, giving the quite good qualitative agreement with experiment (figure 2).

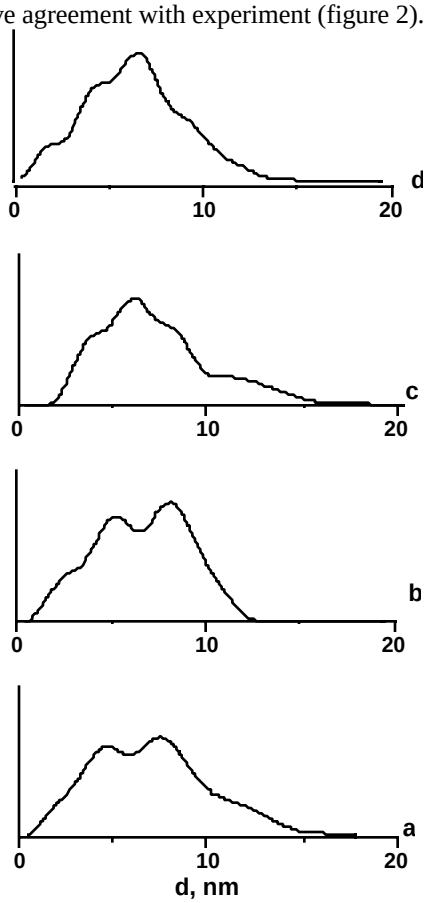

Figure 2. Functions $D_m(d)$ for sensitized samples and for model particles, computed by homogeneous spheres (the functions are normalized on height): a-sensitization time is 2 hours, b-cone with a diameter of the basis 12 nm and height 5.6 nm, c-sensitization time is 15 minutes, d-trihedral pyramid with length of an edge in the basis 14 nm and height 5.6 nm.

We shall notice, that it would be possible to achieve much best concurrence of model function with experimental if to take also into account at simulation a possible disorder on both the sizes and form. However, received even under condition of strict monodispersity the qualitative similarity of model and experimental $D_m(d)$ is represented, in our opinion, rather indicative and allows to make the certain assumptions about morphology of scattering particles. After sensitization process during 2 hours the SAXS intensity, and accordingly, the values of $D_m(d)$ function increase about twice (figure 3). It is remarkable however that the characteristic profile of a $D_m(d)$ curve remains qualitatively the same, that it is possible to interpret as a conservation of morphological peculiarities of scattering particles. If the rise of intensity is connected with increase of quantity of scattering particles, it means that each initial cluster must cause the formation of one more particle similar to the first by the size and the form.

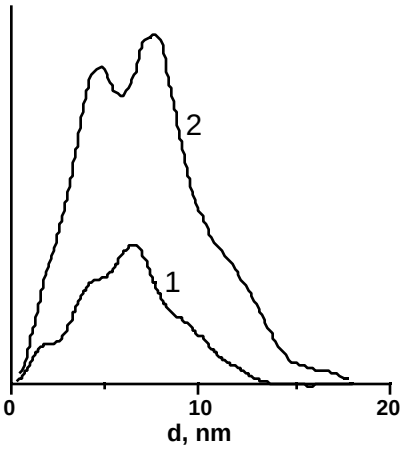

Figure 3. Rise of function $D_m(d)$ by the sensitization process: a-sensitization time is 15 minutes, b-sensitization time is 2 hours.

Much more logical, in our opinion, to explain the observable phenomenon by change of contrast, that is, increase of density of scattering particles (it is well known that SAXS intensity is proportional to the square of scattering density fluctuation). It is rather curious that the ratio of SAXS integral intensity values in the initial and the final moment of sensitization process (1:2.07) exactly corresponds to the relation of squares of densities of Ag_2S and silver. This fact allows to assume that a final product of sensitization process by the given technique is nothing else than high-dispersed silver.

References

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