The Synergetic Action of Chemical and Spectral Sensitizations on Cubic {100} AgBr Microcrystals

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Abstract

The given work is devoted to comparative research of influence of adsorption of dye on a surface of cubic {100} AgBr microcrystals, subjected to various types of chemical sensitizations, on a level of photographic sensitivity and optical density of the fog of photographic layers on their basis.

Influence of the nature thyacarbocianin Dyes on sensitometric characteristics of photographic layers with the centers of photographic sensitivity received at sulfur, sulfur – plus - gold, reduction and reduction – plus - gold chemical sensitizations is investigated.

It has been established, that the level of photographic sensitivity and optical density of the fog of photographic layers is determined by the nature of a spectral sensitizer besides adsorption of some dyes results in decrease in optical density of the fog. Investigating efficiency of a spectral sensitization of cubic {100} AgBr microcrystals depending on type of the centers of photographic sensitivity, mutual influence of chemical and spectral sensitizations has been shown.

Introduction

One of most important aspects in modern photographic practice is the search of the techniques of improving of efficiency of the photographic process on halide silver (AgHal) microcrystals (MC) to increase photographic materials' sensitivity. The most important stages for effective formation of the photographic speed surface centers are chemical and spectral sensitizations. The process of spectral sensitization is a less investigated and more interesting method of photographic speed increase in AgHal MC. One of the difficulties in achieving the highest photographic speed during spectral sensitization is the desensitization effect of secondary oxidation-reduction processes of Dye (D). Therefore, to achieve the highest photographic speed it is necessary to eliminate these processes.

It is common knowledge that the fog optical density values of a photographic layer at spectral sensitization always increase [1]. However, on the basis of our experimental data it was found out that the introduction of certain carbocyanine D on tabular MC reduces the fog optical density values achieved during chemical sensitization [2] without photographic speed decrease and the maximum optical density of darkening decrease. The goal of the paper is to determine the influence of the chemical nature of impurity centers (IC) on spectral sensitization by one and the same Dye.

Experiment

Synthesis of the photographic emulsion

The emulsion containing cubic AgBr MC with the average equivalent diameter d = 0,80 mcm and the variation factor C_v = 8% was synthesized by the two-jet crystallization method [3]. The electronic microphotograph of the emulsion is given in Fig. 1.

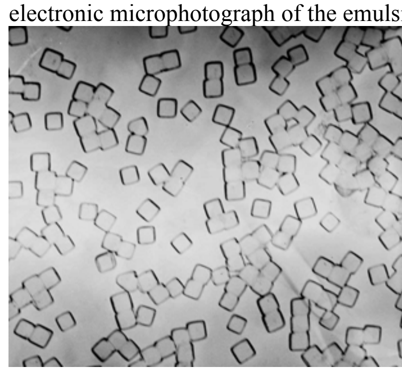


Figure 1. *The electronic microphotograph of cubic AgBr MC.*

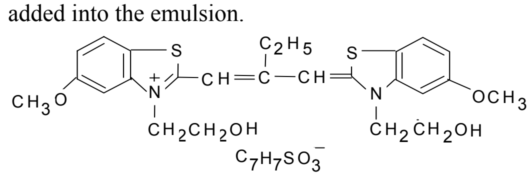
Chemical sensitization (CS)

IC of the different chemical nature ($(Ag_2S)_nAg_mAu_k$, $(Ag_2S)_nAg_m$, Ag^0_n, $Ag^0_nAu_k$) were formed on the surface of cubic AgBr MC by means of different types of CS. The conditions for CS AgBr MC were adjusted for each type of CS. Four types of CS resulting in IC of the different chemical nature were investigated, namely: sulfur CS ((S)-CS) by $Na_2S_2O_3$, sulfur-plus-gold CS ((S+Au)-CS) by $Na_2S_2O_3$ and $HAuCl_4$, reduction CS ((Sn)-CS) by $SnCl_2x2H_2O$ and reduction-plus-gold CS ((Sn+Au)-CS) by $SnCl_2x2H_2O$ and $HAuCl_4$.

The conditions for sensitizations and the sensitometric characteristics of the photographic layers (relative photographic speed (S_{rel}), fog optical density values (D_0) and maximum density of darkening values (D_{max})) are submitted in Table.

Spectral sensitization (SS)

To determine the degree of the influence of the chemical nature of IC on SS by the same Dye during CS, the Dye (D-1) was added into the emulsion.



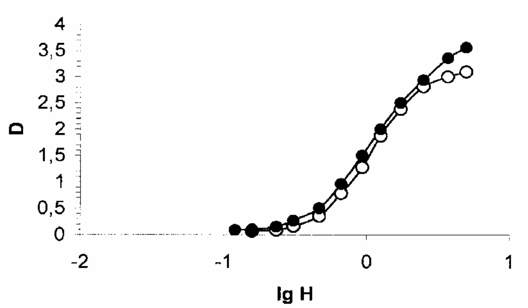
Dye-1

The D-1 concentration in the emulsion was $6{,}2x10^{-5}$ mole/mole Ag. After the adsorption of D-1 onto the surface of cubic AgBr MC with the IC of the different chemical nature, the photographic layers were coated on the support. Then, chemically and spectrally sensitized photographic layers were subjected to sensitometric tests and the photographic speed and fog optical density values were compared. The values of the photographic characteristics of the emulsion layers are submitted in Table. The characteristic curves of chemically and spectrally sensitized photographic layers for different types of CS are presented in Fig. 2.

Sensitometric characteristics and the conditions for chemical and spectral sensitizations of the photographic emulsion:

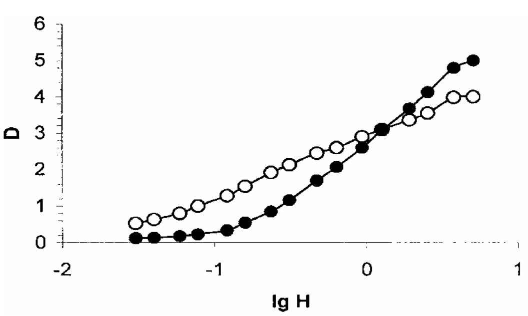
CS additives, x 10^{-5} mole/mole Ag			Sensitometric characteristics received at CS			Sensitometric characteristic received at SS by D-1		
$[Na_2S_2O_3]$	$[HAuCl_4]$	$[SnCl_2]\times 2H_2O$	S_{CS}	D_0	D_{max}	S_{SS}	D_0	D_{max}
7,2	-	-	20	0,18	3,11	30	0,17	4,89
7,2	1,7	-	30	0,33	4,53	50	0,14	5,11
-	-	5,4	10	0,30	2,51	40	0,45	4,42
-	1,7	5,4	25	0,39	3,73	100	0,88	4,55

These characteristic curves show the influence of Dye-1, depending on the type of chemical sensitization, on photographic speed of cubic AgBr MC.



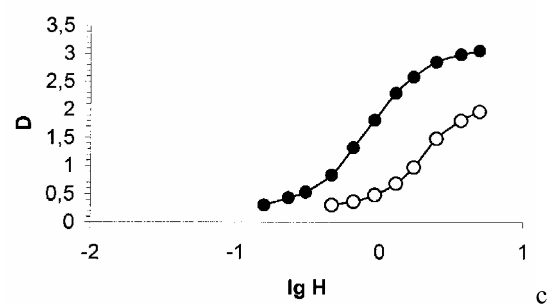
a

○ - the sample after sulfur CS,
● - the sample after sulfur CS and adsorption of D-1



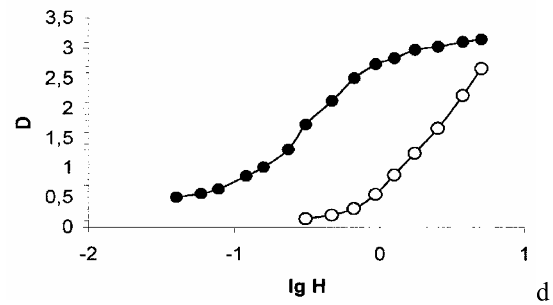
b

○ - the sample after sulphur –plus - gold CS,
● - the sample after (S+Au)-CS and adsorption of D-1



c

○ - the sample after reduction CS,
● - the sample after reduction CS and adsorption of D-1



d

○ - the sample after reduction-plus-gold CS,
● - the sample after (Sn+Au)-CS and adsorption of D-1

Figure 2. *Characteristic curves of photographic layers with IC received for different types of CS.*

Based on the experimental data, photographic speed increase values (S) due to adsorption of D-1 during CS for different types of IC were calculated. S was calculated by the formula: $S = S_{SS} - S_{CS}$, where: S_{CS} - photographic speed received at CS; S_{SS} - photographic speed received at SS.

The values of S are submitted in Fig. 3.

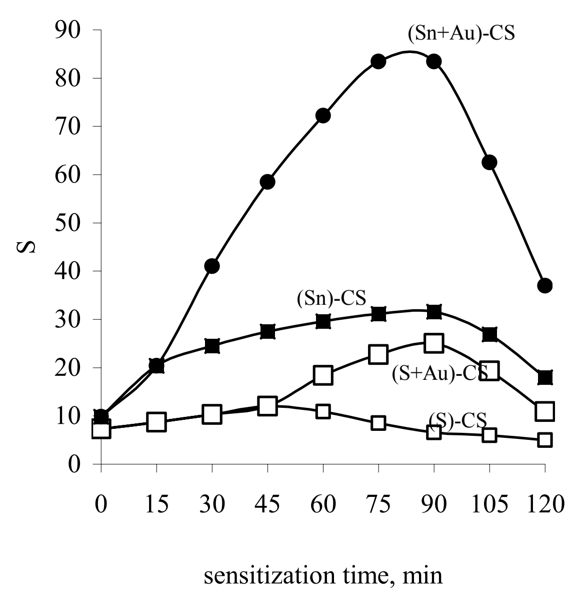


Figure 3. *Dependence of photographic speed increase (S) from the time of sensitization after adsorption of D-1.*

It is seen that the dependence of photographic speed increase on the time of sensitization after adsorption of D-1 for different types of CS is extreme to a greater or lesser extent with the exception of (S)-CS for which insignificant increase in photographic speed is observed during the first 45 min. During (S+Au)-CS appreciable photographic speed increase (~ two-fold increase) occurs within 30-90 min followed by photographic speed decrease due to fog optical density increase. During (Sn)-CS there occurs gradual increase of S (for 90 min) followed by its decrease due to fog optical density increase. Sharp increase in photographic speed during (Sn+Au)-CS occurs from the first minutes of the introduction of $HAuCl_4$ and proceeds for 90 min. Thus, (Sn+Au)-CS allows us to receive the maximum absolute photographic speed increase during SS. On the other hand, from the CS data (see Table) it is evident that the reduction sensitization is least effective. (S)-CS allows us to obtain photographic speed values twice as much as the values during (Sn)-CS. The inclusion of gold atoms into the structure of IC results in photographic speed increase both for (Sn)-CS and for (S)-CS, and there occurs two-fold increase in fog optical density during (Sn)-CS. Thus, the best sensitometric characteristics are achieved during (S+Au)-CS.

The experimental data show that the influence of adsorption of D-1 on IC, having a different chemical nature, on photographic speed can be different depending on the IC type.

During (S)-CS and (S+Au)-CS the adsorption of D-1 does not actually affect photographic characteristics of the layers because of desensitization. Our experimental data agree to the data [4] on weak SS of Ag_2S centers by cyanine D. Desensitization effect, in this case, is explained by the recombination of photoelectrons and holes of D on Ag_2S centers. However, during (S+Au)-CS fog optical density values after the adsorption of D-1 decrease.

The interaction of D-1 with the Ag^0 centers formed during (Sn)-CS appeared more effective. It is known that photographic layers with the (Sn)-CS centers are least subjected to desensitization by D [1]. Silver clusters (the centers of (Sn)-CS) are the acceptors of both electrons and holes depending on their size [5]. A characteristic property of (Sn)-CS is its ability of forming a great amount of inner electron and hole traps in spite of the fact that the inclusion of gold into the structure of IC stabilizes silver clusters and catalyses their development but photographic speed values of the layers with the Ag^0 and $Ag^0{}_nAu_k$ centers remain low (see Table). However, these centers eliminate the desensitization effect caused by D-1. For the photographic layers with the $Ag^0{}_nAu_k$ centers there was observed six-fold increase in photographic speed at rather high fog optical density values.

Hence, the optimum photographic properties cannot be obtained when using only one type of IC. To exclude the desensitization effect caused by D we decided to use mixed sensitization, viz, $Na_2S_2O_3$, $HAuCl_4$ and $SnCl_2x2H_2O$ were used as chemical sensitizers. In this case $SnCl_2x2H_2O$ acted as a reductone*.

The characteristic curves showing a consecutive change of the photographic response of the layers depending on the conditions for mixed (Sn+S+Au) sensitization are submitted in Fig. 4.

*One of the methods of overcoming the desensitization effect caused by D is to carry out SS in the presence of reductones [1, 6] i.e. substances possessing the reducing properties.

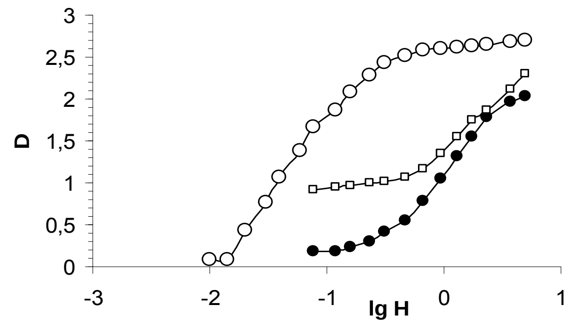


Figure. 4. *Characteristic curves of chemically (□ - (S+Au)-CS, ● - (Sn+S+Au)-CS) and spectrally (○ - (Sn+S+Au)-CS + D-1) sensitized photographic layers.*

It is seen that characteristic curves after the application of $SnCl_2$ $2H_2O$ as a reductone, fog optical density values decrease significantly. The adsorption of D-1 results in further decrease in fog optical density and, thereby, in appreciable layer photographic speed increase. The method proposed for this type of sensitization is rather perspective since high photographic speed values are achieved by systematically decreasing fog optical density values.

Conclusion

Having investigated the efficiency of spectral sensitization of cubic AgBr MC depending on the type of photographic speed centers, it is shown that chemical and spectral sensitizations influence each other. Also, it was found out that the introduction of Dye reduces fog optical density values achieved at (S+Au)- and (Sn+S+Au)-CS if they are not too high. The impurity centers - $Ag^0{}_n$, $Ag^0{}_nAu_k$ during spectral sensitization are least subjected to the desensitization effect caused by Dye.

It is stated that sensitizers and dyes for each photographic material should be thoroughly selected to achieve the optimum photographic characteristics.

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Author Biography

Juliya N. Afonkina was born in Kemerovo (Russia) on June 25, 1980. In 2002 graduated from the State University of Kemerovo, Chemistry Faculty. Since 2002 she worked on General Physics departments of Kemerovo State University as a Scientific Researcher. Now she is Post-graduate student of the General Physics department of Kemerovo State University. Her field of research is chemical sensitization processes of silver halide photographic emulsions. The author of 23 scientific publications.